polymers

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Supplementary Materials:

Chitosan-Sulfated Titania Composite Membranes with Potential Applications in Fuel Cell: Influence of Cross-Linker Nature

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Determination of molecular weight of chitosan

Molecular weight of the chitosan was determined using an Ubbelohde viscosimeter (Oa capillary, K = 0.005 mm^2/s^2) at 25 ± 0.05 °C. Chitosan was dissolved in an aqueous solution of 2% acetic acid and 0.2 M sodium acetate (1/1 V/V) to obtain different chitosan concentrations (0.02; 0.04; 0.06; 0.08; 0.1; 0.12 and 0.15 g/dL). To ensure the equilibration of the polymer solution, the solutions were kept for 24 hours at 30 °C. The molecular weight was calculated with Mark-Houwink Equation (S1) by using $k = 13.8\cdot\times 10^{-5}$ and $a = 0.85$ (*Kasaai, Carbohydrate Polymers 68 (2007) 477–488*).

$$[\eta] = k \cdot M_v^a \tag{S1}$$

$[\eta] = intrinsic\ viscosity$
k and a = Mark-Houwink parameters
M_v = average viscosity molecular weight

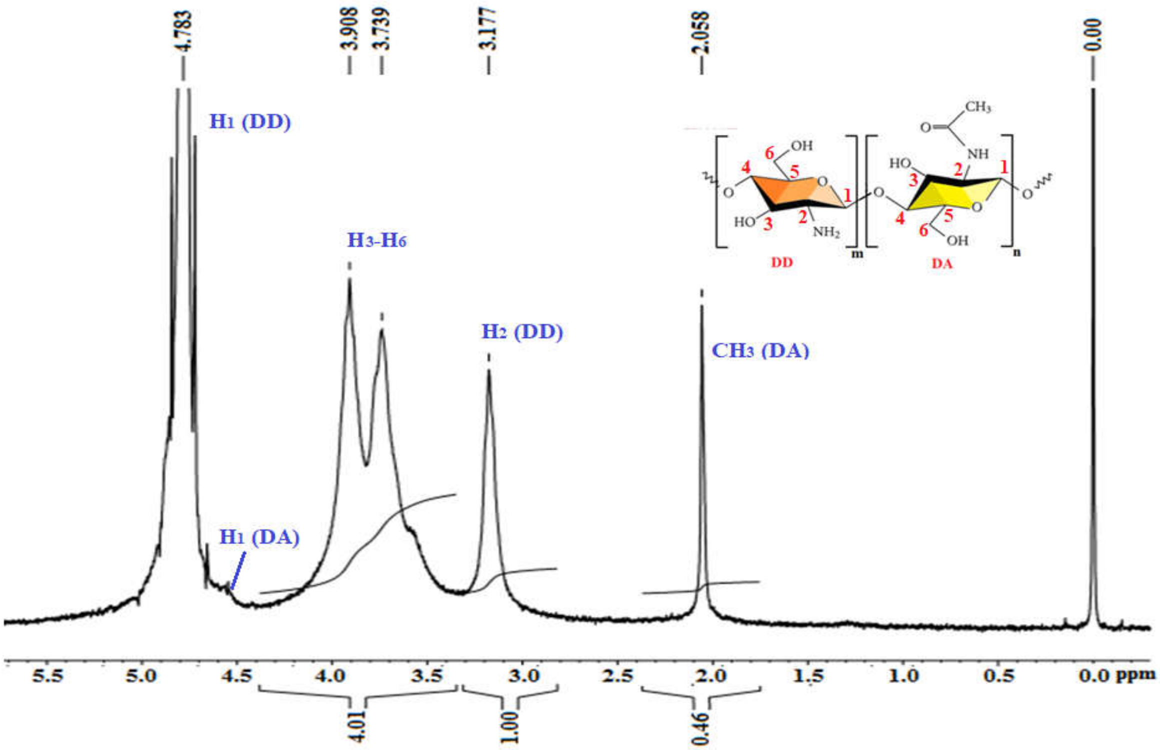

Figure S1. ^{1}H NMR spectrum of pristine chitosan (CS).

The degree of deacetylation (DD) was calculated by using the integral intensity, I_{CH3}, of the CH_3 residue, and the sum of integral intensities, $I_{H2\text{-}H6}$, of H2, H3, H4, H5 and H6 proton:

$$DD(\%) = (1 - (I_{CH3\text{-}DA}/3)/(I_{H2\text{-}H6}/6))\bullet 100$$

In our particular case, the degree of deacetylation was calculated as follows:

$$DD = (1 - (0.46/3)/(5.01/6)) \times 100 = 81.94\%$$

Determination of sulfate groups content by back-titration method

The content of sulfate groups was determined by a common back titration method: Shortly, the sulfated titania particles were suspended in a NaOH solution of known concentration and the suspension was stirred for 2 h for neutralization of sulfate groups and filtrated. The unreacted NaOH was titrated with HCl solution in the presence of phenolphthaleine. The content of sulfate groups/g particles was calculated with Equation S1.

$$Sulfate\ groups\ content\ \left(\frac{mol}{g}\right) = (V_{NaOH} \cdot C_{NaOH} - V_{HCl} \cdot C_{HCl})/m \qquad (S2)$$

where: V_{NaOH} (mL) and C_{NaOH} (Eq/mL) are the volume, respectively the concentration of NaOH solution used to neutralize the sulfate groups; V_{HCl} (mL) and C_{HCl} (Eq/mL) are the volume, respectively the concentration of HCl solution used to titrate the reacted NaOH solution; m (g) is the mass of sulfated titania particles.

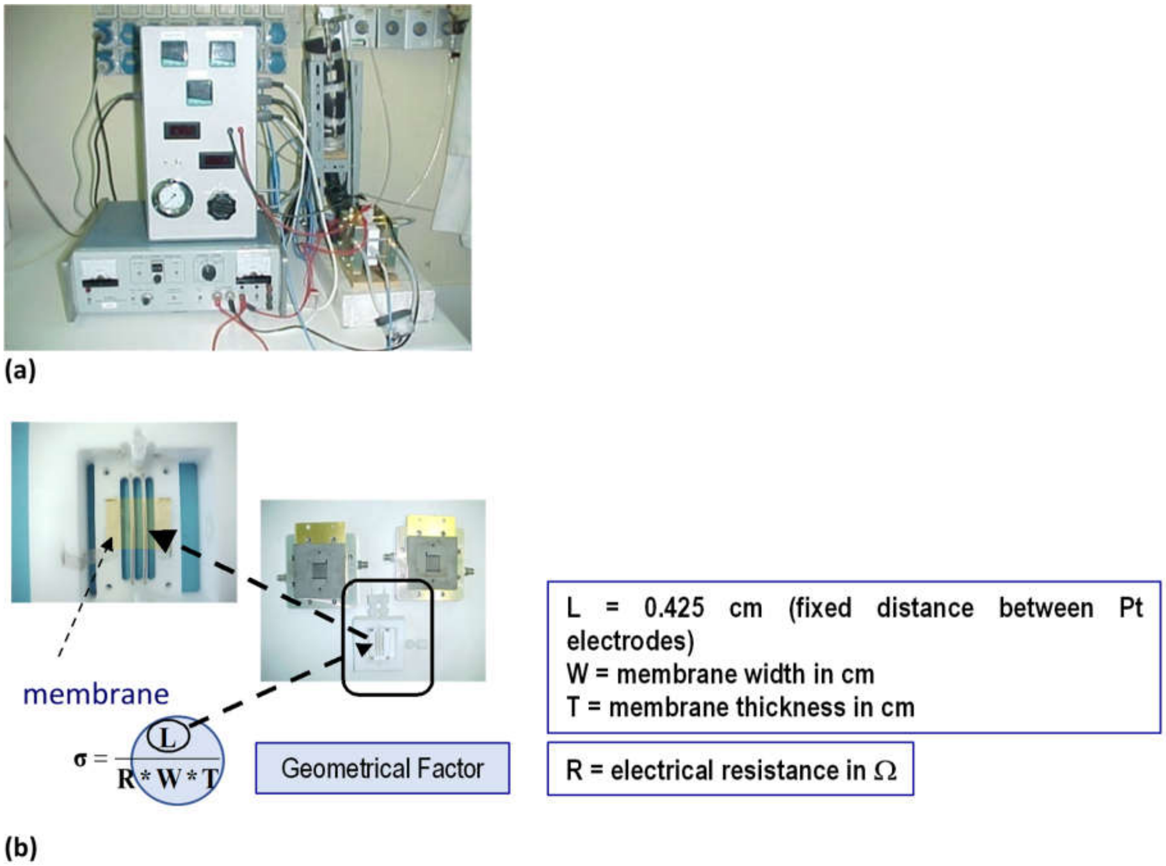

Figure S2. (**a**) Test station for proton conductivity measurement connected to cell and potentiat-galvanostat; (**b**) conductivity cell and formula used.

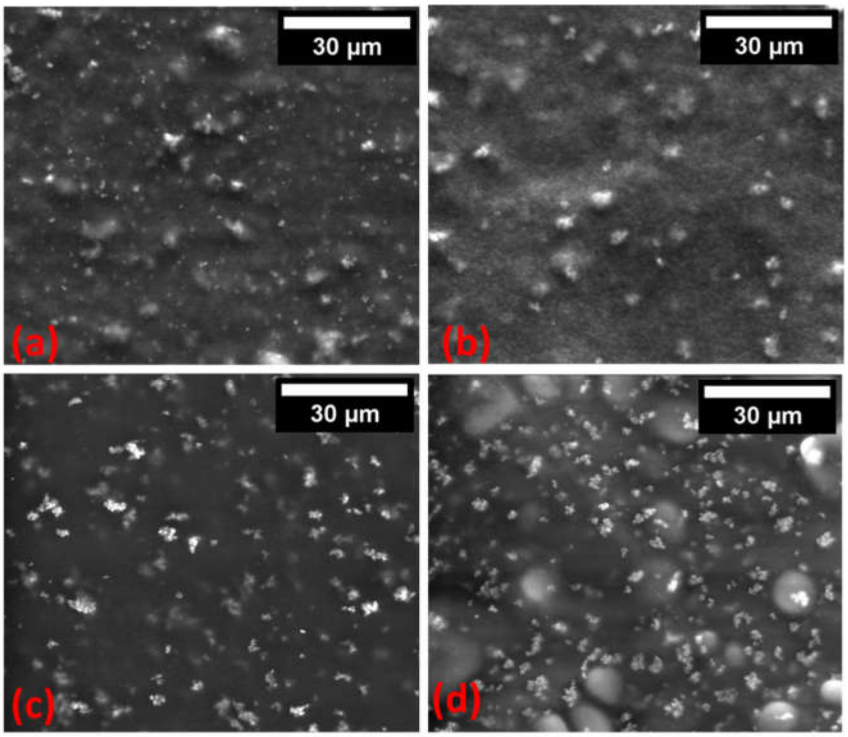

Figure S3. Representative surface SEM images of (**a**) composite chitosan – sulfonated titania membrane (CS-TS) and composite chitosan – sulfonated titania membranes cross-linked with (**b**) sulfuric acid, (**c**) pentasodium tripolyphosphate and (**d**) polydimethylsiloxane (CS-TS-HS, CS-TS-TPP and CS-TS-PDMS, respectively).

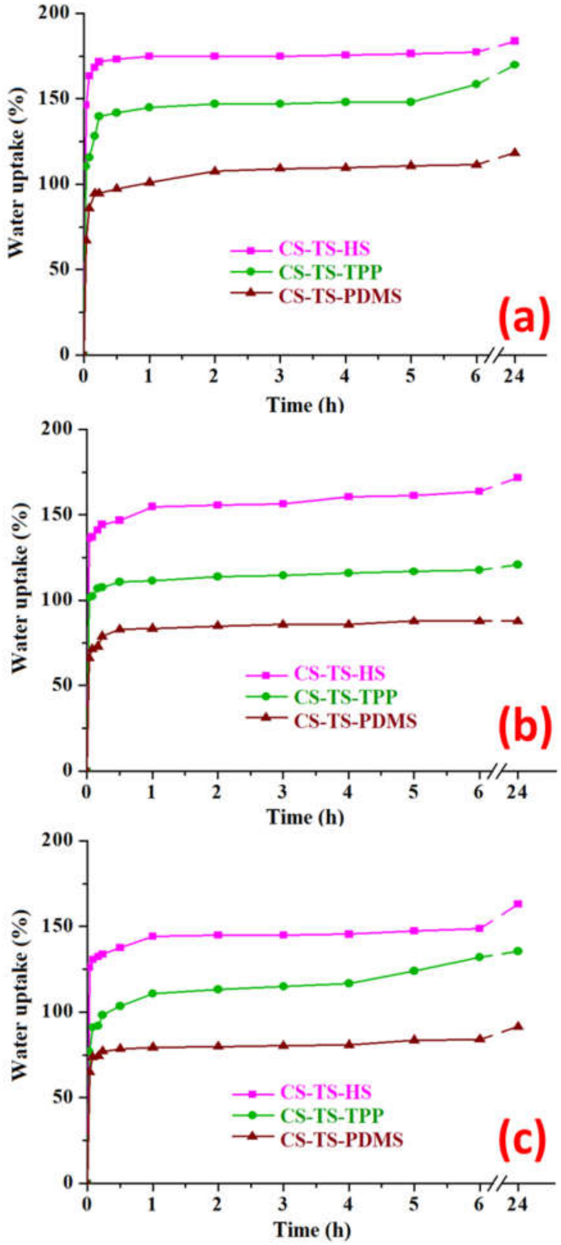

Figure S4. Water uptake kinetics of composite chitosan – sulfonated titania membranes cross-linked with sulfuric acid, pentasodium tripolyphosphate and polydimethylsiloxane (CS-TS-HS, CS-TS-TPP and CS-TS-PDMS, respectively) at (**a**) 25°C, (**b**) 60°C and (**c**) 80°C.

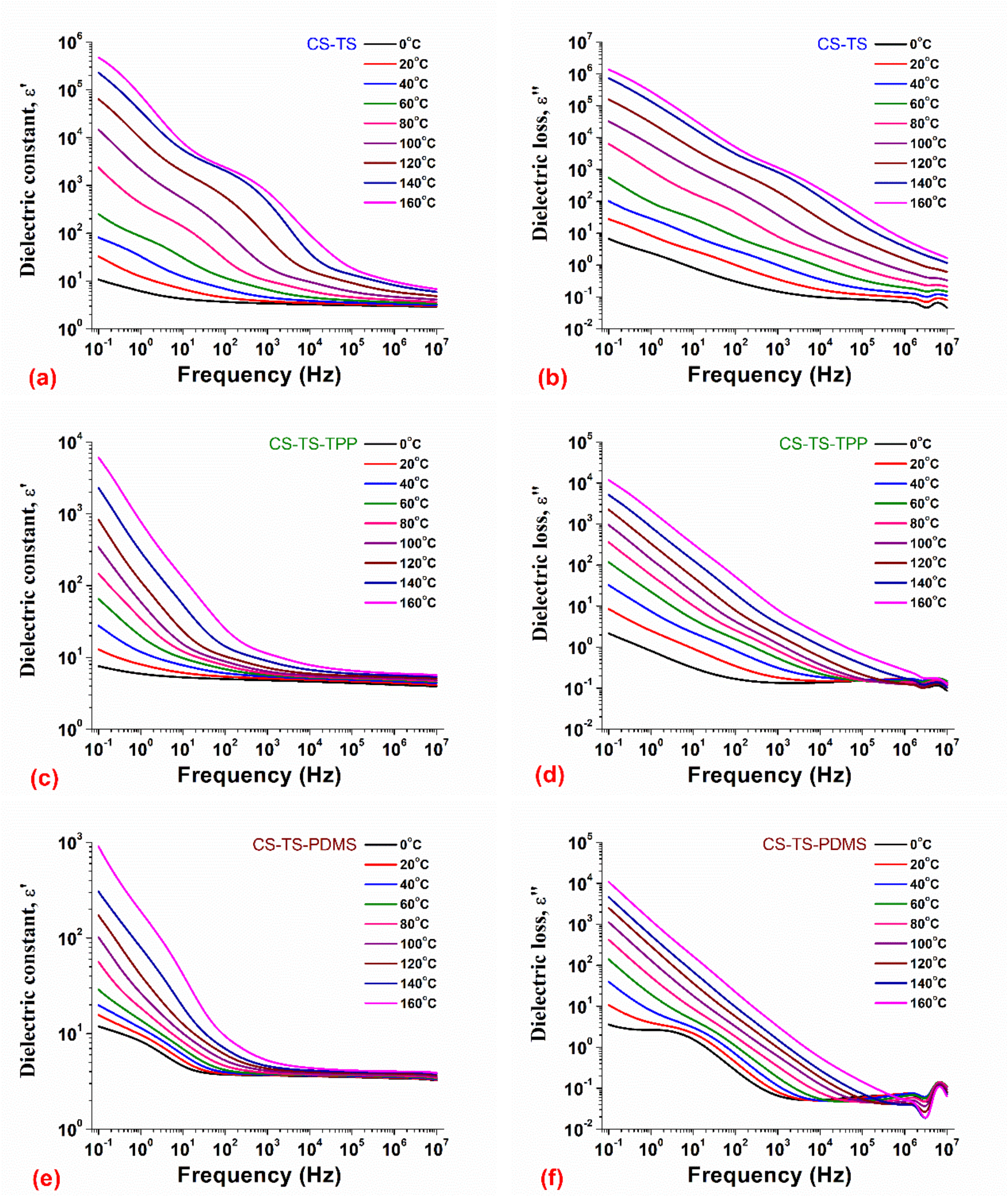

Figure S5. Dielectric constant (**a**,**c**,**e**) and dielectric loss (b,d,f) evolution with frequency for dry CS-TS, CS-TS-TPP and CS-TS-PDMS composite membranes.

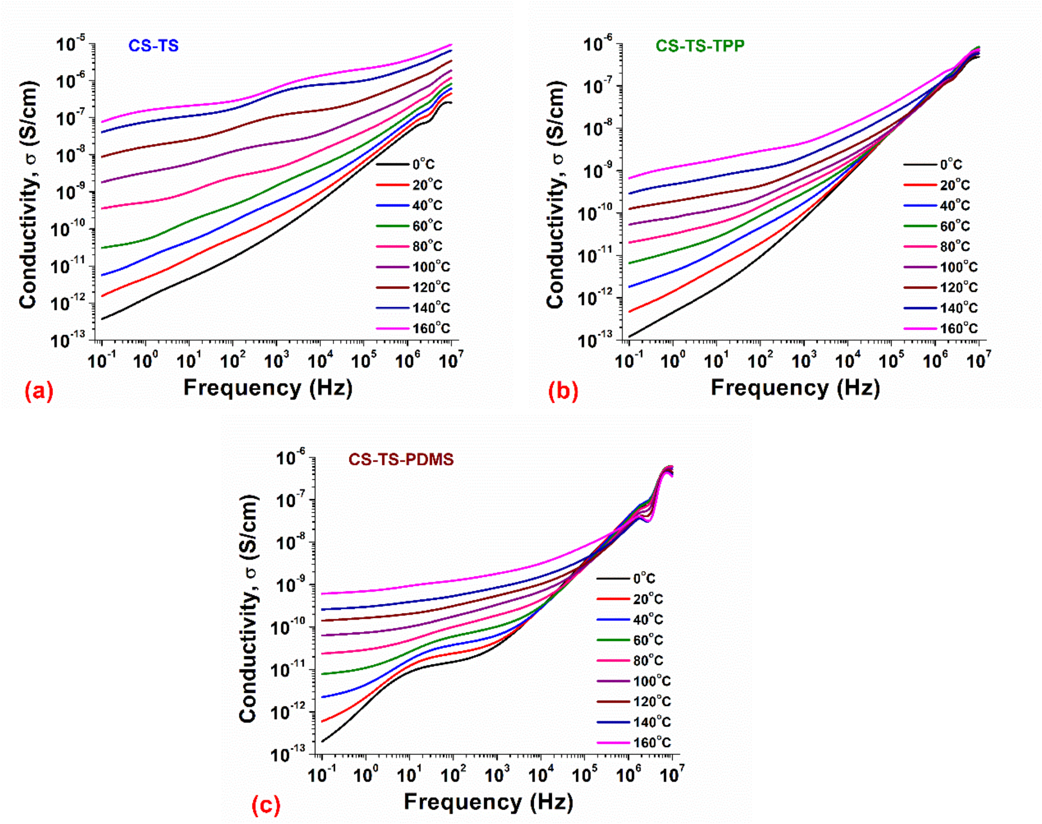

Figure S6. Evolutions of the measured conductivity with frequency for dry (**a**) CS-TS, (**b**) CS-TS-TPP and (**c**) CS-TS-PDMS composite membranes.

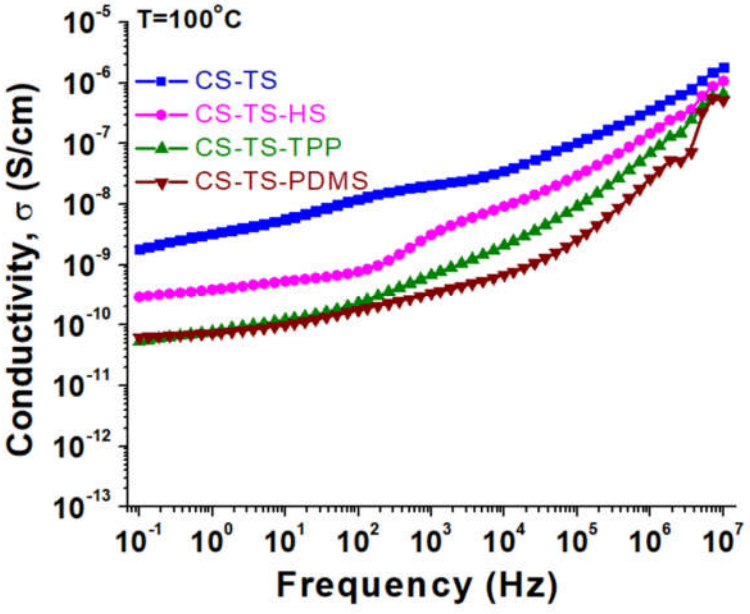

Figure S7. The evolution of conductivity with frequency at 100°C for dry membranes.

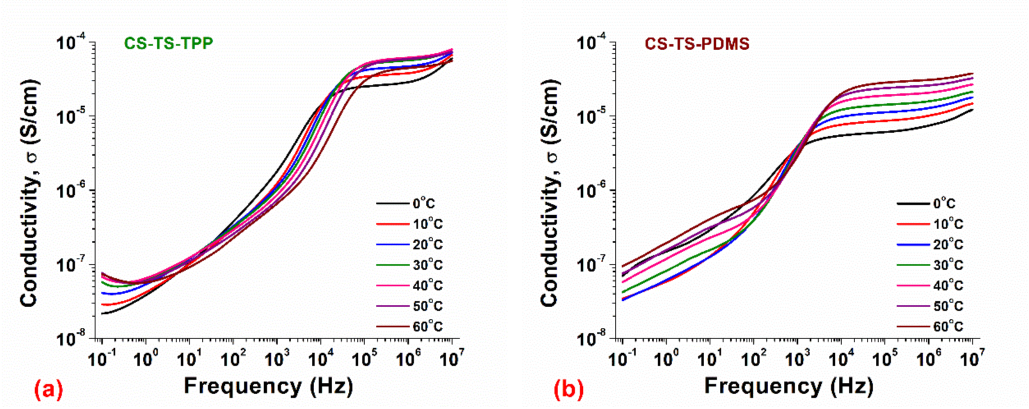

Figure S8. Evolutions of the measured conductivity with frequency for hydrated (**a**) CS-TS-TPP and (**b**) CS-TS-PDMS composite membranes.

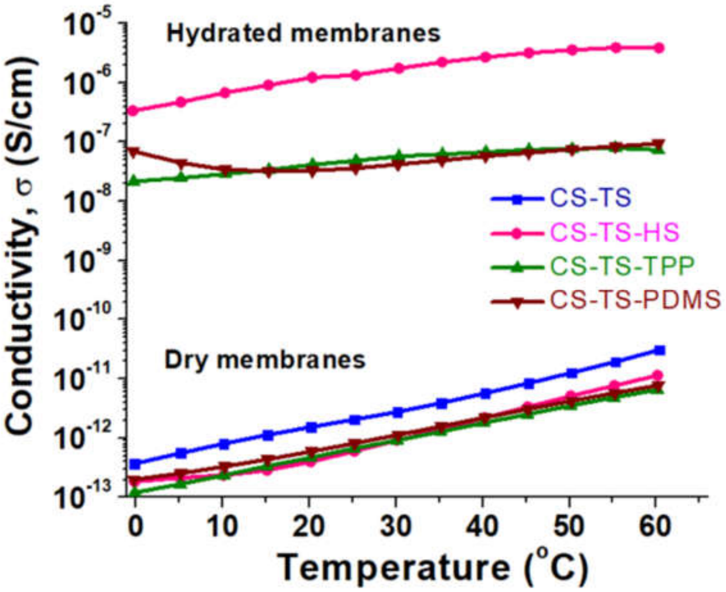

Figure S9. The evolution of conductivity with temperature at 0.1 Hz for dry and hydrated membranes.