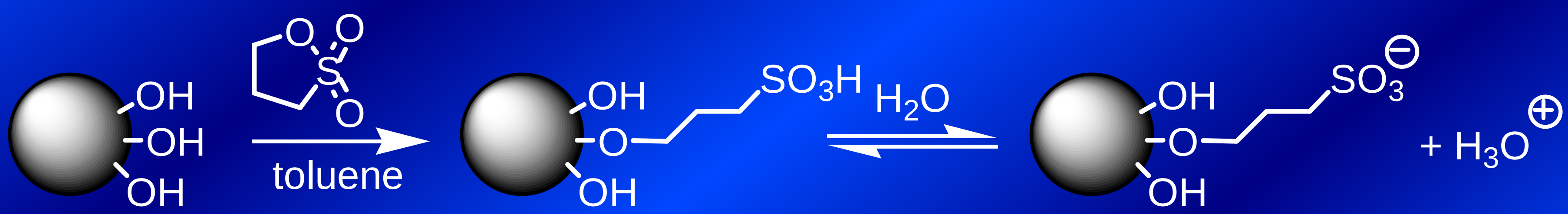
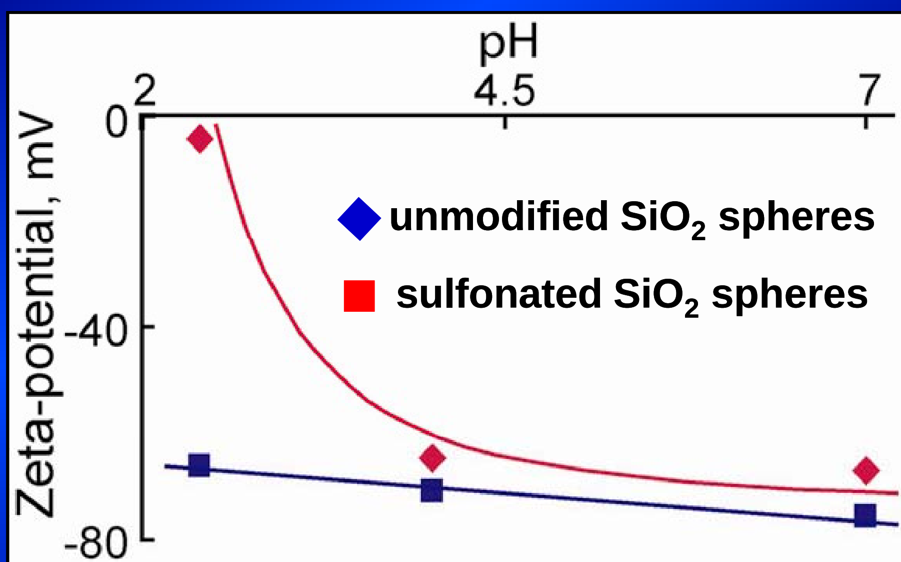
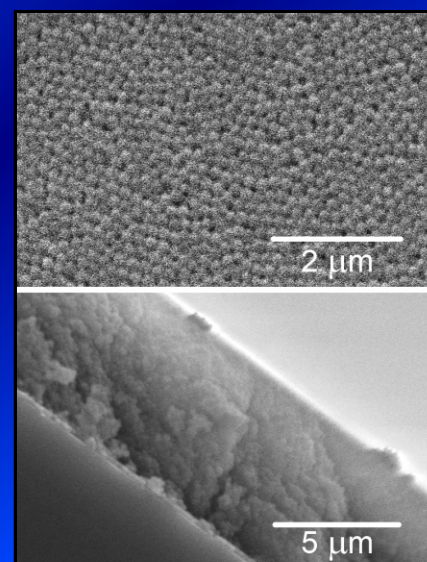
unmodified silica has no strongly acidic groups, surface sulfonation would:

- **provide highly acidic groups**
- **lead to proton-conductivity through interconnected nanopores**







sulfonated silica spheres can be self-assembled into colloidal films

Smith, J. J.; Abbaraju, R, R.; Zharov, I. *J. Mater. Chem.* **2008**, accepted.

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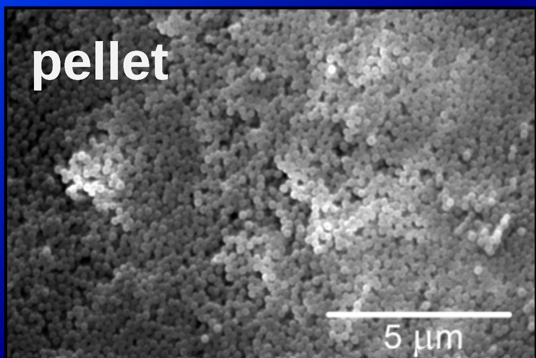
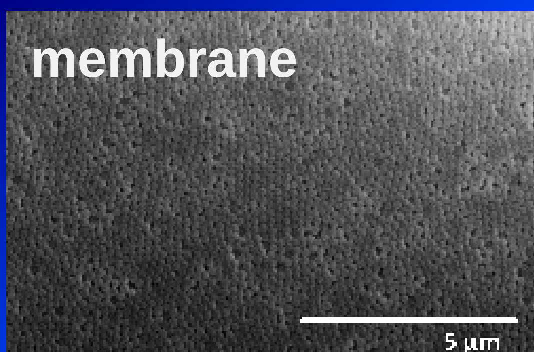
proton conductivity in sulfonated colloidal materials

- ***pellets*** - pressed sulfonated spheres
- ***membranes*** - self- assembled sulfonated spheres
- materials coated with silver, placed between electrodes inside controlled temp/humidity chamber, conductivity is measured using EIS





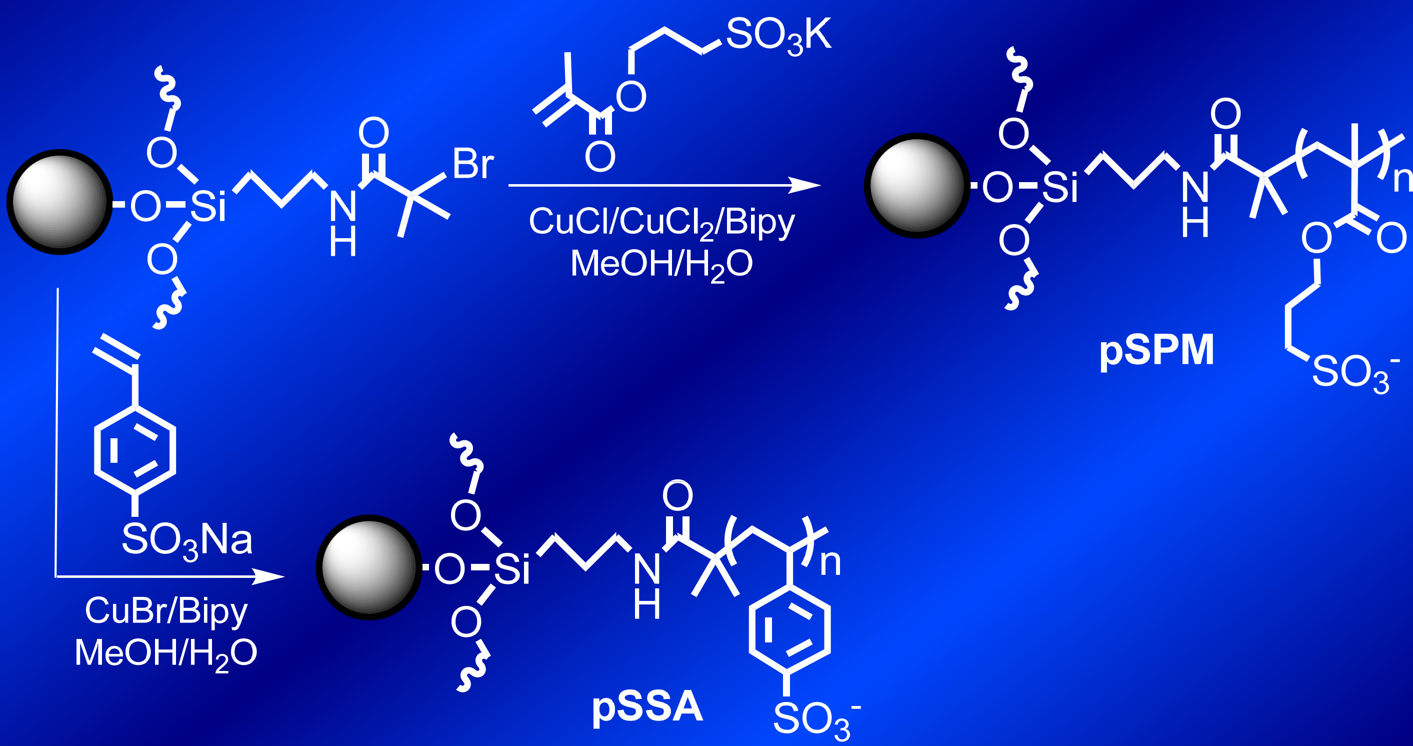
material	proton conductivity σ, S/cm (at 100 ºC and 98% R.H.)	
	unmodified	sulfonated
pellet	2.2×10^{-6}	7.0×10^{-5}
self-assembled membrane	5.0×10^{-6}	1.4×10^{-2}

- ***pellets***: **sulfonation increases proton conductivity ~30-fold, it is comparable to that of some porous glasses but quite low**
- ***membranes***: **ordering of unmodified spheres increases proton conductivity ~2-fold but for sulfonated spheres this increase is *~2 orders of magnitude***

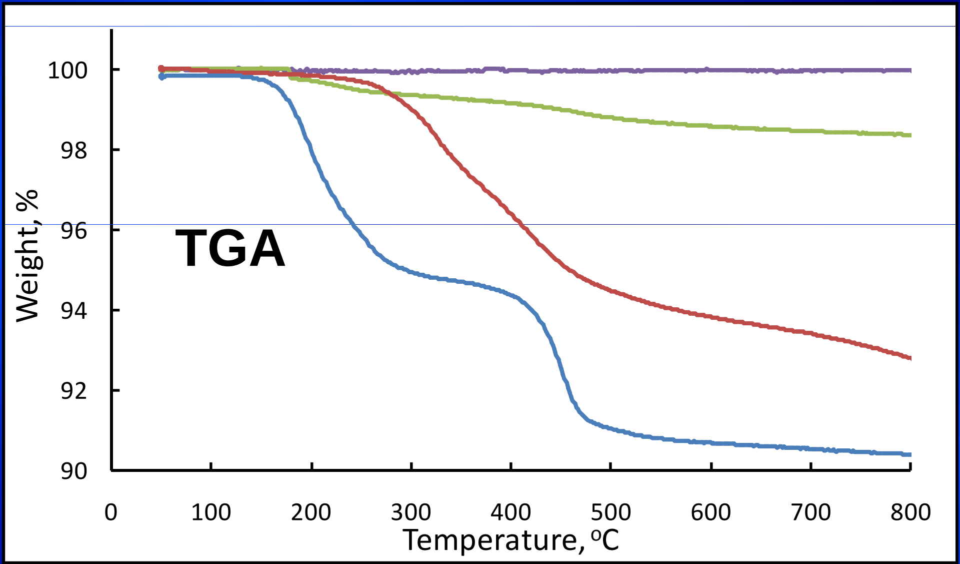
Smith, J. J.; Abbaraju, R, R.; Zharov, I. *J. Mater. Chem.* **2008**, accepted.

novel approach to hybrid proton-conducting membranes:

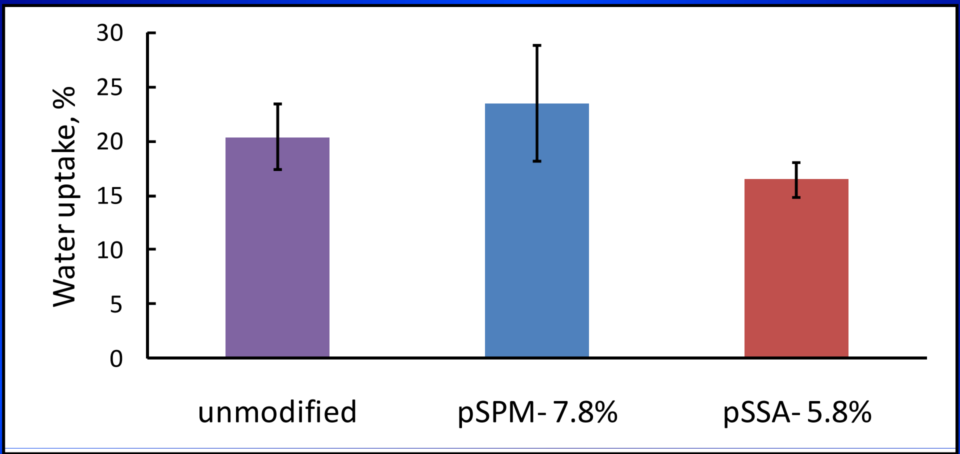
- nano-frit is an inorganic matrix with continuous network of nanopores providing mechanical stability and water retention
- surface-bound polymer brushes with acidic groups provide the proton conductivity
- matrix allows to introduce and investigate unprecedented polymer brush architectures
- inorganic matrix provides mechanical stability under oxidative conditions and high temperature



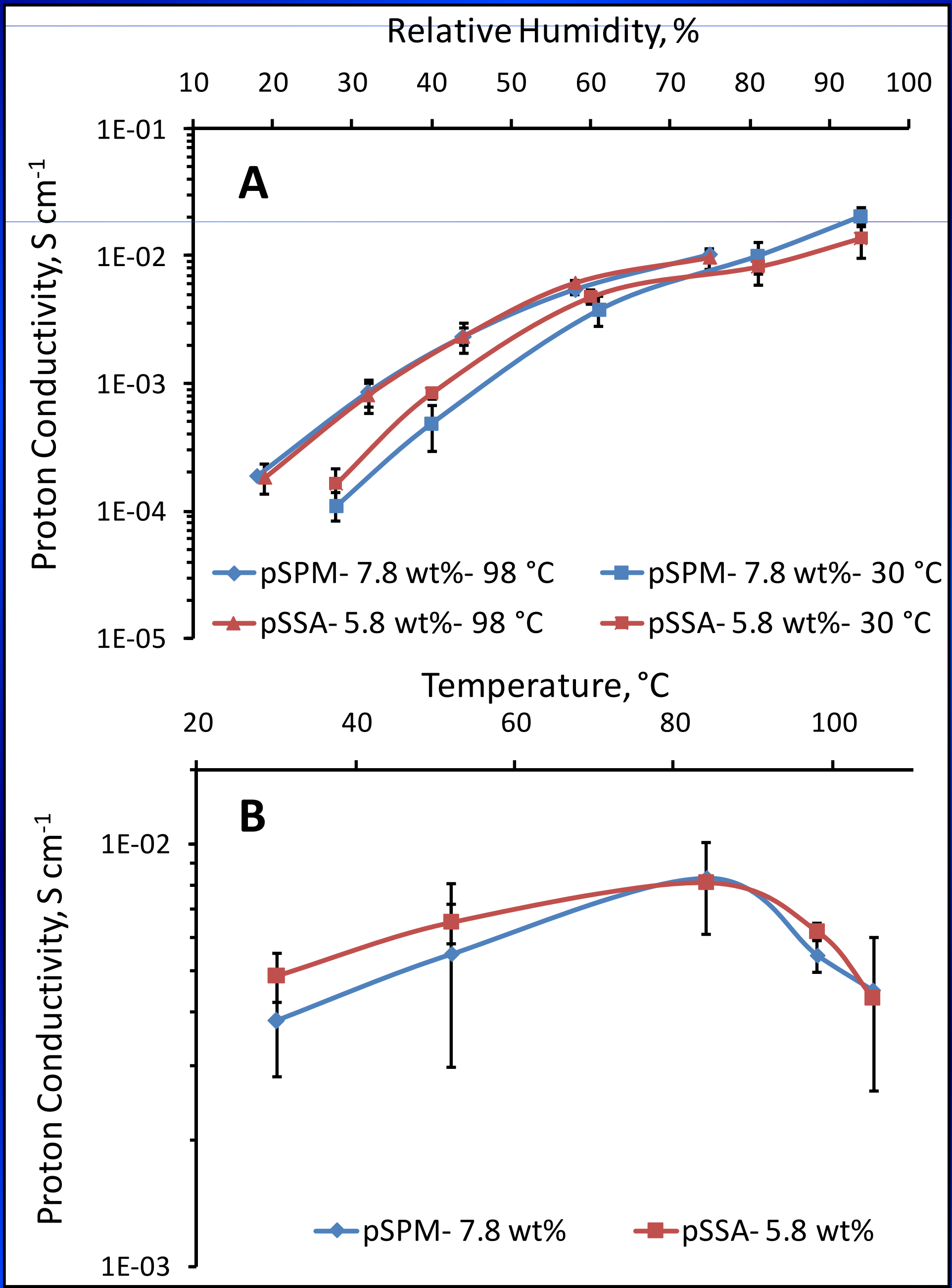
Smith, J. J.; Zharov, I. *Chem. Mater.* **2008**, submitted.



unmodified (purple), initiator-modified (green), pSSA modified (red), and pSPM modified (blue) sintered membranes



water uptake for sintered membranes after soaking in water at room temperature for 24 hours.



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