

Performance Optimization of Polymer Materials Thanks to Sol-Gel Chemistry for Fuel Cells

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Abstract : Proton Exchange Membrane Fuel Cells (PEMFCs) seems to be a promising device used for converting hydrogen into electricity. PEMFC is made of a Membrane Electrode Assembly (MEA) composed of a Proton Exchange Membrane (PEM) sandwiched by two catalytic layers. Nowadays, specific performances are targeted in order to ensure the long-term expansion of this technology. Current polymers used (perfluorinated as Nafion®) are unsuitable (loss of mechanical properties) for the high-temperature range. To overcome this issue, sulfonated polyaromatic polymers appear to be a good alternative since it has very good thermomechanical properties. However, their proton conductivity and chemical stability (oxidative resistance to H₂O₂ formed during fuel cell (FC) operating) are very low. In our team, we patented an original concept of hybrid membranes able to fulfill the specific requirements for PEMFC. This idea is based on the improvement of commercialized polymer membrane via an easy and processable stabilization thanks to sol-gel (SG) chemistry with judicious embedded chemical functions. This strategy is thus breaking up with traditional approaches (design of new copolymers, use of inorganic charges/additives). In 2020, we presented the elaboration and functional properties of a 1st generation of hybrid membranes with promising performances and durability. The latter was made by self-condensing a SG phase with 3(mercaptopropyl)trimethoxysilane (MPTMS) inside a commercial sPEEK host membrane. The successful in-situ condensation reactions of the MPTMS was demonstrated by measures of mass uptakes, FTIR spectroscopy (presence of C-Haliphatics) and solid state NMR ²⁹Si (T₂ & T₃ signals of self-condensation products). The ability of the SG phase to prevent the oxidative degradation of the sPEEK phase (thanks to thiol chemical functions) was then proved with H₂O₂ accelerating tests and FC operating tests. A 2nd generation made of thiourea functionalized SG precursors (named HTU & TTU) was made after. By analysing in depth the morphologies of these different hybrids by direct space analysis (AFM/SEM/TEM) and reciprocal space analysis (SANS/SAXS/WAXS), we highlighted that both SG phase morphology and its localisation into the host has a huge impact on the PEM functional properties observed. This relationship is also dependent on the chemical function embedded. The hybrids obtained have shown very good chemical resistance during aging test (exposed to H₂O₂) compared to the commercial sPEEK. But the chemical function used is considered as "sacrificial" and cannot react indefinitely with H₂O₂. Thus, we are now working on a 3rd generation made of both sacrificial/regenerative chemical functions which are expected to inhibit the chemical aging of sPEEK more efficiently. With this work, we are confident to reach a predictive approach of the key parameters governing the final properties.

Keywords : fuel cells, ionomers, membranes, sPEEK, chemical stability

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