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# BEYOND NAFION®: FUNCTIONALIZED GRAPHENE OXIDE AS A POTENTIAL SELF-ASSEMBLING PROTON-CONDUCTING MEMBRANE FOR PEM FUEL CELLS

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The core of proton exchange membrane fuel cells (PEMFCs), and one of the components in which they can be extensively improved, is their proton-conducting electrolyte. Nowadays, Nafion® is the most widely used material and allowed PEMFCs to establish themselves as the leading commercial-scale fuel cell technology. Nonetheless, it requires completely humidified reactant gases and temperatures in the 60–80 °C range to work properly. Additionally, the release of toxic and environmentally persistent per-and polyfluoroalkyl substances (PFASs) during both its production and disposal makes Nafion® at risk of being banned in the coming future. Therefore, the progress of PEMFCs technology inevitably goes through the pursuit of alternative PFASs-free proton conductors, which must also overcome the performance of Nafion® in conditions suffered by this material, but which would increase both water management and kinetics of the redox reaction, i.e., gas humidification lower than 60% and temperatures higher than 60 °C. Thus, this work focused on the preparation of novel self-standing proton-conducting membranes based on functionalized graphene oxide (GO), whose oxygen-bearing moieties provide well-known hydrophilic and self-assembling properties, as well as the possibility of introducing suitable groups that can enhance proton transport. Thus, sulfuric acid and naphthalene sulfonate (NS) molecules were investigated as functionalizing agents, with the aim to insert proton-carrying sulfonic acid groups and obtain either sulfonated graphene oxide (SGO) or graphene oxide-naphthalene sulfonate (GONS) membranes. Moreover, a potential crosslinking additive, i.e., sodium tetraborate decahydrate (SBD), was exploited to try to enhance the structural stability of the most promising SGO specimen and produce a crosslinked SGO-B membrane. Samples with six acid-to-GO, two GO-to-SBD, and three GO-to-NS molar ratios were prepared and analyzed via ATR-FTIR, SEM-EDX, Raman, TGA, XPS, XRD, and by the evaluation of their mechanical behavior, ion exchange capacity (IEC), water uptake, and in-plane proton conductivity ($\sigma_{ip}$). The last two features were explored at 42%, 53%, and 95% humidification in the 20–100 °C range. These tests allowed the identification of three most promising membranes, i.e., SGO-10, GONS-5-T100, and SGO-B80 A, which exhibited 4.2, 2.9, and 4.7 meq/g, respectively, of IEC, and 1.15, 1.71, and 0.19 S/cm, respectively, of $\sigma_{ip}$ (at 80 °C, 95% relative humidity), compared to 0.7 meq/g and 0.60 S/cm, respectively, for Nafion® 212. Their production processes were finally analyzed via life cycle assessment and SGO-10 stood out among all GO-based membranes, due to its remarkable proton transport along with the best mechanical properties and carbon footprint.