Development of novel proton conducting membranes based on self-assembling borate-reinforced sulfonated graphene oxide

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Several materials were studied to adequately replace Nafion® as proton exchange membrane in the homonymous fuel cells (PEMFCs), aspiring at enhancing their performances at high temperatures and low humidity [1]. Amongst them, graphene oxide (GO) and its sulfonated derivatives (SGO) attracted remarkable interest [2] due to their ability to assemble freestanding and proton-conducting membranes. Previous studies demonstrated the promising properties of SGO membranes prepared with sulfuric acid as sulfonating agent, but also highlighted their fragility and difficult handling [3]. This work aims at fabricating innovative SGO membranes with ameliorated mechanical stability by enriching them with sodium tetraborate decahydrate (SB) as crosslinking agent [4,5]. SGO-SB membranes were prepared combining a GO aqueous dispersion and concentrated H_2SO_4 in controlled amounts to perform the sulfonation of GO as the first step. The mixture was magnetically stirred at 25 °C for three hours and at 100 °C for additional three hours before being cooled down at room temperature. Afterwards, SB was added and the resulting mixture was stirred for further 15 minutes, diluted with deionised water, vacuum filtered and oven-dried at 40 °C to manufacture the membranes. Eventually, annealing was performed at 90 °C to activate the formation of crosslinks among GO flakes. Five GO/SB molar ratios (40, 60, 80, 100, 120) and four annealing times (50, 100, 150, 200 min) were tested, in order to comprehend both optimal membrane composition and treatment conditions. The prepared samples were characterised by XRD, ATR-FTIR, Raman and EDX spectroscopies, SEM, TGA and ion exchange capacity (IEC) evaluation to assess the effect of the insertion of sodium tetraborate groups on the functionalities of pristine GO and on its ability to exchange ions. This analysis helped to identify the optimal GO/SB molar ratio and annealing time. XRD analysis indicated an interlayer spacing increase at higher SB content possibly due to the steric hindrance of the inserted molecules, which seemed to prevent a strong crosslinking. However, longer annealing times appeared to be favourable. The highest IEC was identified at the lowest GO/SB molar ratio, but in this case shorter annealing times guaranteed better performances. The sulfonated membranes with the most promising combination of GO/SB ratio and annealing time underwent further water uptake (WU) and electrochemical impedance spectroscopy (EIS) tests at different temperature and humidity values to evaluate their potentiality as novel proton conductors for PEMFCs. Mechanical tests are ongoing and more precise results will be shown during the conference.

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