Infrared spectroscopy study on self-standing functionalized graphene oxide membranes to be used as novel proton conductors in PEM fuel cells

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This work has developed innovative membranes based on graphene oxide (GO) functionalized with sulfonic acid groups ($–SO_3H$) analogous to those of Nafion®, a perfluorosulfonate ionomer that is currently the most common electrolyte in the field of proton exchange membrane fuel cells (PEMFCs). They have been evaluated as a potential alternative to Nafion®, in order to achieve a superior operation at elevated temperatures and reduced humidification, which are extremely detrimental conditions for its performance and mechanical stability [1].

Sulfonated graphene oxide membranes (SGO) have been prepared by reacting a commercial, aqueous GO dispersion with different volumes of sulfuric acid, in order to assess their effect on both structure and degree of functionalization of the electrolytes. They have been characterized by FTIR, XRD and SEM-EDX spectroscopies, optical microscopy, thermogravimetry and static contact angle studies. These tests allowed to determine an optimal sulfonation ratio, which has been identified from an empirical formula of GO derived, as a first approximation, from the elemental analysis of the commercial dispersion. The water uptake, ion exchange capacity (IEC) and degree of sulfonation of the electrolytes have been evaluated as well, and a correlation among them has been established. SGO membranes have exhibited enhanced water uptake and ion exchange abilities with respect to both Nafion® and virgin GO; in particular, an IEC value above 1 meq g^{-1} has been detected, higher than the ones reported for Nafion® (≈ 0.9 meq g^{-1}) [2]. Then, a preliminary test in a lab-scale hydrogen-fed fuel cell has been performed on a specimen corresponding to a 1:1 acid-to-GO molar ratio. This resulted in an open circuit voltage (0.63 V) lower than the theoretical maximum value of 1.23 V and than the one of 0.9-1 V usually measured for Nafion®, probably due to hydrogen crossover issues. However, the membrane also showed a promising resistance to compression and to contamination by carbon residues left by the gas diffusion electrode, which are a typical issue in the case of Nafion®.

Infrared spectroscopy has been fundamental to confirm the successful functionalization of GO, as witnessed in the spectra of SGO membranes taken with both KBr disc and ATR methods, displaying new bands compatible with the stretching vibrations of $–SO_3H$ moieties. However, the surface analysis provided by the latter also suggested that a probable reduction and amorphization of GO's framework has been induced by the proposed sulfonation procedure. Specific samples have been examined directly in transmission, in order to provide a comparison between surface and bulk, the latter revealing a different distribution of functionalities and a higher degree of structural disorder. ATR-FTIR spectra have been taken as well after water uptake and fuel cell tests, resulting in a good stability of sulfonated moieties after the exposure to a hot, humid atmosphere. The harsher environment of the fuel cell caused instead the removal of less stable oxygenated functions (lactols, peroxides) and major changes in the surface composition, ascribed to the action of the fluxing gases, while the bulk exhibited a better stability.

References:

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