High temperature proton exchange membranes based on polybenzimidazoles for fuel cells
- DTU Orbit (14/08/2019)

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To achieve high temperature operation of proton exchange membrane fuel cells (PEMFC), preferably under ambient pressure, acid–base polymer membranes represent an effective approach. The phosphoric acid-doped polybenzimidazole membrane seems so far the most successful system in the field. It has in recent years motivated extensive research activities with great progress. This treatise is devoted to updating the development, covering polymer synthesis, membrane casting, physicochemical characterizations and fuel cell technologies. To optimize the membrane properties, high molecular weight polymers with synthetically modified or N-substituted structures have been synthesized. Techniques for membrane casting from organic solutions and directly from acid solutions have been developed. Ionic and covalent cross-linking as well as inorganic–organic composites has been explored. Membrane characterizations have been made including spectroscopy, water uptake and acid doping, thermal and oxidative stability, conductivity, electro-osmotic water drag, methanol crossover, solubility and permeability of gases, and oxygen reduction kinetics. Related fuel cell technologies such as electrode and MEA fabrication have been developed and high temperature PEMFC has been successfully demonstrated at temperatures of up to 200 °C under ambient pressure. No gas humidification is mandatory, which enables the elimination of the complicated humidification system, compared with Nafion cells. Other operating features of the PBI cell include easy control of air flowrate, cell temperature and cooling. The PBI cell operating at above 150 °C can tolerate up to 1% CO and 10ppm SO2 in the fuel stream, allowing for simplification of the fuel processing system and possible integration of the fuel cell stack with fuel processing units. Long-term durability with a degradation rate of 5Vh–1 has been achieved under continuous operation with hydrogen and air at 150–160 °C. With load or thermal cycling, a performance loss of 300V per cycle or 40Vh–1 per operating hour was observed. Further improvement should be done by, e.g. optimizing the thermal and chemical stability of the polymer, acid–base interaction and acid management, activity and stability of catalyst and more importantly the catalyst support, as well as the integral interface between electrode and membrane.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry, Energy and Materials, Case Western Reserve University
Contributors: Li, Q., Jensen, J. O., Savinell, R. F., Bjerrum, N. J.
Pages: 449-477
Publication date: 2009
Peer-reviewed: Yes

Publication information
Journal: Progress in Polymer Science
Volume: 34
Issue number: 5
ISSN (Print): 0079-6700
Ratings:
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 11.539 SNIP 8.141
Web of Science (2009): Indexed yes
Original language: English
Keywords: Durability, Polybenzimidazole (PBI), Cross-linking, Fuel cell, Phosphoric acid, High temperature proton exchange membrane
Electronic versions:
2009 PBI review Progress in Polymer Science 34, 5, 449-477.pdf
DOIs:
10.1016/j.progpolymsci.2008.12.003
Source: orbit
Source-ID: 232784
Research output: Contribution to journal › Journal article – Annual report year: 2009 › Research › peer-review