LOW TEMPERATURE PROTON CONDUCTING MEMBRANES FOR FUEL CELL APPLICATIONS: FROM NAFION TO UP TO DATE MATERIALS

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Introduction

There is a stable tendency of transition from classic fuel cells with liquid electrolyte to solid state electrolyte fuel cells and from high to low temperature for portable current sources in the world for last years. Nafion type membranes are usually used in such devices. They are an advanced technology products but those gas-permeability is quite low.

Perfluorochemical membranes

Nafion type perfluorochemical polymers have different arrangement and amount of fluorinated and sulphuretted parts of polymer chain and are fabricated by few enterprises (Du Pont, Asahi, Dow). Films made out of these polymers have globular structure and have quite large amount of cavities formed by electronegative groups repulsion. This cavities are filled up with grate amount of water in its media because of its interaction with hydrophilic SO_3H fragments. The continuous proton hydrate shell is formed when some critical level of water filling is reached. The proton formed by sulfonate group dissociation is transferred in this shell. The conductivity fails at temperature higher then 373 K. It is caused by water evaporation. Hydrophobic part of this polymer provides good mechanical stability even at water absence and hydrated hydrophilic parts provide high proton conductivity (better then 10^{-3} S/cm at room temperature) at water presence higher then 30 % mass. But the conductivity greatly depends on environment humidity because of hydrophilic sulfonate groups fixed on polymeric base. Nearly all molecules of water are included in hydrogen bonds system so they are able to take part in proton transport. H-binding in fully hydrated Nafion is much weaker then in liquid water. Membranes conductivity greatly depends on water presence and shows anisotropic effect: tangential component of conductivity of swollen membrane is $8.6 \cdot 10^{-2}$ S/cm at 100%RH and perpendicular component is $2.4 \cdot 10^{-2}$ S/cm at the same conditions.

But such membranes own proton conductivity is very low and effective proton transport is determined by presence of water adsorbed from air. That is why such membranes should work at continuous humidification and heating in fuel cells. Furthermore the membranes synthesis is quite hard procedure that is why the price of high-quality membranes is high. The disadvantages of such membranes also are low thermal stability, low hydrogen ionization and oxygen reduction reaction speeds on the Nafion-electrode material border. The power of fuel cell based on Nafion can reach up to 400-700 mW/cm^2 at 353 K and 100 % RH.

Sulphuretted polymers

Another way to obtain proton conducting membrane based on aromatic condensed polymer is different type polymers sulfonation, synthesis based on sulfonate group containing monomers, sulfoalkylated substitutes introduction. Such polymer electrolytes are rigid chain polymers with low proton conductivity at water absence. The proton conductivity of hydrated polymer electrolytes strongly rises and reaches 10^{-1} - 10^{-2} S/cm at water amount increasing. The use of sulphuretted polymer electrolytes in fuel cells is restricted by those destruction caused by desulphurization process at temperatures higher then 473 K. Thermally stable polymers are obtained by sulfoalkylated substitutes introduction in to macromolecules of aromatic polymers. Those electrochemical characteristics can be controlled by changing number of substitutes and alkyl chains length. Sulfoalkylated polymers can have dehumidification and proton conductivity close to sulphuretted electrolytes: it is typical for them to have high thermal and chemical stability and also mechanical strength. The solubility of such polymers in organic dissolvers depends on sulfoalkylation depth. Absorbed molecules of water are better held by sulfoalkylated then perfluorochemical polymers. The membranes based on sulfur-fluorinated polystyrene (BAM3G) are produced by Ballard Advanced Materials

Corporation and are used in fuel cells manufacturing.

Gel-electrolytes and composite proton conducting systems

The materials, conductivity in which is carried out by dissociation of low-molecular compounds in dissolver introduced in to polymer matrix can be related to special group of electrolytes. For example strong organic acids (fluoroacetic, sulfonic acid) introduction in to Nafion type or sulphuretted polymers leads to proton transfer possibility in more wide range of humidity. Inorganic acids ($HClO_4$, H_2SO_4, H_3PO_4, H_3PO_2 and $H_3PW_{12}O_{40}$) are introduced in to inert matrix (polyethylene oxide, polyethylene glycol, polycarbonates) or in to polymer able to form strong hydrogen bonds (polyamides, alcohols, acids). The values of conductivity can be reached up to 10^{-2} - 10^{-3} S/cm in both cases but strong conductivity dependence on environment humidity is observed in first case. The proton transfer is carried out with polymer matrix fragments movement in dry atmosphere and by its own proton hydration shell in wet one. Low mechanical strength is a common disadvantage of such type materials.

Polybenzimidazole based proton conducting membranes (PBI)

All described earlier polymers keep high ionic conductivity only at temperatures up to 373 K because the conductivity is carried out by proton hydration shell formed by adsorbed water. The several number of proton conducting membranes based on PBI is developed and manufactured for higher temperatures applications. The own conductivity of PBI is very low but its chemical modification made it possible to obtain membranes with acceptable transport properties. Thermally stable proton conducting polymers consisting of PBI and strong acids (H_3PO_4, H_2SO_4 и HCl) are synthesized. It was discovered that PBI and strong acid films form polymer complexes by H-binding and acid-alkali interactions between imidazole groups of PBI and water molecules. It was shown that they behave like electrolytes with ionic transport carried out by segment polymer movement.

Polymer electrolyte membranes based on PBI doped by H_3PO_4 in range 300 – 1600 mol % are used in fuel cells at temperature range 423 - 473 K. It was shown that conductivity of such polymers is not sensitive to environment humidity but greatly depends on acid doping depth and reaches up to 0.13 S/cm at 433 K. But the mechanical properties of such membranes fail at doping depth rising.

PBI membrane doped by H_3PO_4 620 mol % works in fuel cell without air and hydrogen humidification. The maximum power is 0.55 W/cm^2 at 1.2 A/cm^2 current density, 463 K and atmosphere pressure.

Sulfopropylalated or sulphuretted PBI is cheaper and thermally stable material then Nafion. The maximum water absorption is up to 11.3 H_2O per sulfonate group at 90 % RH and room temperature and the conductivity is 10^{-3} S/cm at 293 – 413 K. The water molecules connected with SO_3^- stay in polymer at higher temperatures unlike free water. High sulphuretted PBI keeps enough water amounts that promote conductivity at more high temperatures. Fuel cells based on such polymer membranes yield power about 300 mW/cm^2 at 353 K, 100 % RH current 0.8 A/ cm^2 and cell voltage 0.38 V.

PBI - H_3PO_4 membranes are produced by Celanese enterprise and are used for mid temperature fuel cells manufacturing.