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Effect of the nature of functional groups grafted on the surface of silica nanoparticles on properties of the hybrid proton-conductive membranes based on N-phosphorylated polybenzimidazole

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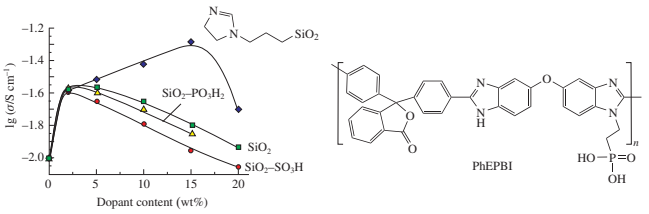
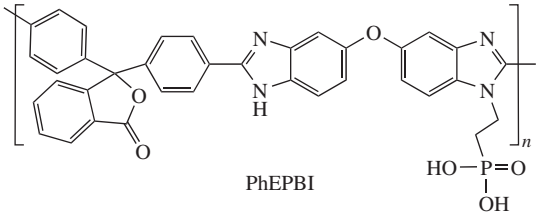
New hybrid proton-conductive membranes containing incorporated silica nanoparticles and modified with various functional groups have been designed, prepared and evaluated for conductive properties. The best conductivity (54 mS cm^{-1} at 130 °C) was reached for membranes doped with silica (15 wt%) bearing grafted imidazolinopropyl groups that favor additional sorption of phosphoric acid.

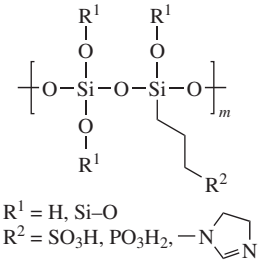


The search for new highly conductive membranes possessing an enhanced thermal stability to be applied in fuel cells is a problem of current interest. Polybenzimidazole doped with acids is among the promising polymers. However, its use at temperatures below 160 °C is limited due to leaching of the acid and decreasing in the conductivity. This drawback has already been fixed *via* an incorporation of inorganic particles to stabilize acids (*e.g.*, inorganic oxides)[1–3] or grafting acidic groups onto the polymer.[4] Phosphonic groups provide a number of advantages over sulfonic ones, *e.g.*, the former are less dependent on the humidification and more chemically and thermally resistant due to the high strength of C–P bond.[5] In comparison with sulfonic groups, a transfer of protons in such polyelectrolytes is possible along the system of hydrogen bonds that are formed even at low humidity without any participation of water molecules.[6] An incorporation of oxides, whose surfaces were modified by acidic or basic groups, can tune the properties of membranes more efficiently.[7–9]

The present work was aimed at the creation and evaluation of the properties of hybrid membranes based on N-phosphorylated polybenzimidazole (PhEPBI, degree of phosphorylation is 92%) and silica bearing functional groups of various nature on its surface.



Hybrid membranes were obtained by casting a PhEPBI polymer solution containing precursors for the synthesizing particles according to the method described in details in our previous work.[10] To obtain a surface-modified silica, commercially available organosilanes were used [(3-mercaptopropyl)trimethoxysilane, triethoxy-3-(2-imidazolin-1-yl)propylsilane and (2-diethylphosphatopropyl)triethoxysilane]. In the case of (3-mercaptopropyl) trimethoxysilane, the SH groups were oxidized into SO_3H ones before the silanol groups hydrolysis by immersing the membranes in a H_2O_2 solution (30%) at room temperature for 24 h. Films containing silica (2–20 wt%) with surfaces functionalized by propylsulfonic acid, propylphosphonic acid or imidazolinopropyl groups were prepared, the content of functional groups being 20 mol%. Hereinafter, these oxides are referred as SiO_2–SO_3H, SiO_2–PO_3H_2 and SiO_2–Im, respectively. The obtained membranes were doped with phosphoric acid (50%). The introduction of dopants did not lead to any deterioration of mechanical properties of the membranes in comparison with initial PhEPBI.



Transmission electron microscopy (TEM) data confirmed the formation of silica nanoparticles possessing the sizes of 3–5 nm and uniformly distributed in the polymer matrix (Figure 1). Upon the incorporation of SiO_2–PO_3H_2 and SiO_2–SO_3H, the content of phosphoric acid molecules per formula unit of the polymer (x) decreases with raising the mass fraction of dopant (Table 1). However, in the case of incorporated oxide functionalized with basic groups, the maximum x values were obtained at a low dopant concentration. The above trend for decreasing x values is due to the binding of SiO_2–PO_3H_2 and SiO_2–SO_3H to the nitrogen atoms of PhEPBI, which are responsible for the sorption of phosphoric acid. At the same time, the initial x growth in the case of SiO_2–Im is caused by the incorporation of additional basic nitrogen atoms.

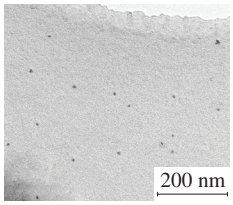


Figure 1 TEM micrograph of the PhEPBI/SiO_2–PO_3H_2-5% membrane.

The conductivity of obtained membranes was estimated by the impedance spectroscopy. The proton conductivity measured at 90 °C grew with increasing the relative humidity (RH). The conductivities of hybrid membranes containing the equal dopant concentrations varied within the measurement accuracy and did not depend on the nature of the grafted functional groups, since the conductivity growth under these conditions is primarily caused by an increased water content due to the higher RH, which results in additional dissociation of phosphoric acid. In this case, the viscosity of the solution within the polymer decreases, while the concentration of carriers increases accelerating the proton transfer.

An evaluation of the temperature effect on the conductivity without any additional humidification revealed that the incorporated dopants enhanced the ionic conductivity of hybrid membranes and its activation energy in comparison with a non-doped sample (Figure 2). In the case of silica containing acid groups, a conductivity jump was observed at the dopant concentration of *ca.* 2 wt%, followed by its gradual decrease with an increase in the concentration of particles [Figure 2(*b*)]. Upon the incorporation of oxide containing imidazoline groups, the conductivity increased up to 54 mS cm^{-1} at 130 °C for the sample with *ca.* 15 wt% content of SiO_2–Im. The conductivity growth in such systems results from the change in the size of pores and channels connecting the pores and is similar to that observed previously.[3] In the case of SiO_2–Im, the grafted functional group is of basic nature and favors a sorption of acid, which is accompanied by increases in the *x* value and the rate of proton transport by the Grotthuss mechanism due to its affinity to the polymer of basic nature and possible participation of the protonated imidazoline particles in the proton transfer chain.

In conclusion, it has been demonstrated that the nature of functional groups considerably affects the transport processes in membranes based on polybenzimidazole. The best properties were achieved in the membranes doped with silica bearing the grafted imidazolinopropyl groups that favor additional sorption of phosphoric acid.

Table 1 Degree of doping of PhEPBI hybrid membranes with phosphoric acid.

Dopant content, ω (wt%)	Dopant, *x*			
	SiO_2	SiO_2–SO_3H	SiO_2–PO_3H_2	SiO_2–Im
0	9.2			
2	8.8	9.1	8.7	11.3
5	8.2	8.1	8.9	10.1
10	7.9	7.4	8.3	9.1
15	7.7	6.9	8.3	8.7
20	7.2	6.6	8.2	8.3

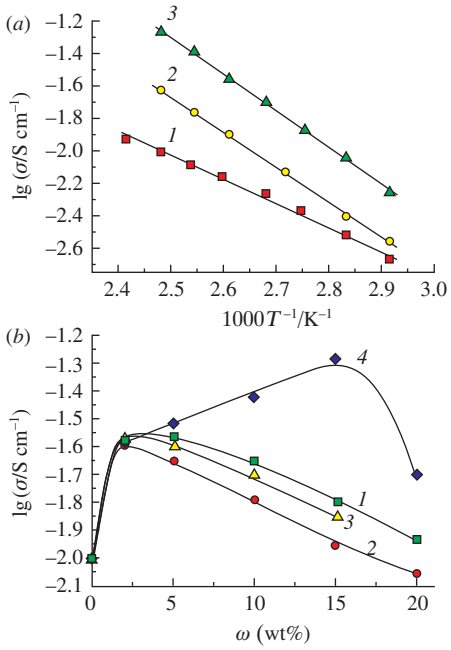


Figure 2 Plots of the conductivity of PhEPBI hybrid membranes (*a*) *vs.* temperature: (*1*) PhEPBI, (*2*) PhEPBI/SiO_2–Im-5%, and (*3*) PhEPBI/SiO_2–Im-15%; and (*b*) *vs.* dopant concentration at 130 °C: (*1*) PhEPBI/SiO_2, (*2*) PhEPBI/SiO_2–SO_3H, (*3*) PhEPBI/SiO_2–PO_3H_2, and (*4*) PhEPBI/SiO_2–Im.

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