

Significant improving H⁺/VO²⁺ permselectivity of Nafion membrane by modification with PDDA in aqueous isopropanol

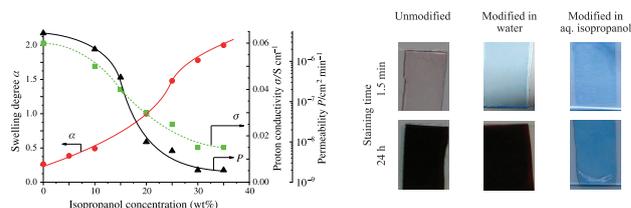
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The modification of Nafion[®] membranes with poly(diallyldimethylammonium chloride) (PDDA) in aqueous solutions of isopropanol has been investigated. A remarkable decrease in vanadyl ion permeability (by 3.5 orders of magnitude), accompanied by a decrease in proton conductivity sixfold at most, was found for Nafion membranes modified in 30–35 wt% isopropanol solutions providing a high swelling of the membranes. The Bradford reagent has been used for the detection of PDDA on the membrane surface.



Keywords: Nafion membrane, PDDA, isopropanol, vanadyl permeability, proton conductivity, Bradford reagent.

Nafion[®] membranes are widely used in the modern fuel cell and redox flow battery industry, including all-vanadium flow batteries, due to their superior mechanical, chemical and thermal stability as well as high proton conductivity.^{1,2} At the same time, Nafion membranes demonstrate a relatively low selectivity which is the main drawback hindering their application as proton-conductive ion-selective separators.

Nafion is a perfluorinated polymer bearing terminal sulfonic groups in its side chains. The structure of the Nafion membrane is still under discussion,^{3–6} the major suggested models being cluster⁴ and layer⁵ ones. In either case, it is accepted that perfluorinated chains are segregated into crystalline regions, while sulfonic groups are concentrated in hydrophilic channels (blobs), providing transmembrane transport of all species and ions. Therefore, the first approach to increase membrane selectivity is associated with narrowing the channels clearance, which is known to reduce the ion flux and improve the membrane selectivity.^{7,8} An alternative approach is related to the creation of a film, providing high vanadium ion (or other species) rejection, on the membrane surface. Different approaches and modification agents developed for the improvement of the membrane selectivity are comprehensively analyzed in the recent reviews.^{2,9–12}

Among many other organic and inorganic modifiers, polyelectrolytes are widely studied ones. Typically, two oppositely charged polyelectrolytes are applied to the membrane surface from aqueous solutions using a layer-by-layer (LBL) technique.^{2,13} However, LBL modification has an insufficient effect on the membrane selectivity.¹³ It is not surprising because the polyelectrolytes applied by LBL are loosely packed,¹⁴ and the resulting film has a poor cutoff effect. Besides, polyelectrolytes absorbed on the membrane surface from aqueous solutions do not penetrate the hydrophilic channels of the membrane and, thus, do not affect the membrane transport properties.

We have recently found that using aqueous isopropanol solutions as a medium providing a high membrane swelling makes it possible to carry out the bulk modification of Nafion membranes with polyaniline.¹⁵

This work aimed to improve the H⁺/VO²⁺ permselectivity of the Nafion membrane by modifying it with a cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) upon enhanced membrane swelling. We performed a one-step modification with the polycation and introduced isopropanol into the aqueous modification medium to increase the Nafion membrane swelling.^{15,16}

To prepare a modified Nafion membrane, we incubated a pretreated¹⁷ water-swollen Nafion 112 membrane (Sigma-Aldrich) in the modification solution for 20–24 h, thoroughly washed with bidistilled water and kept in 2.5 M sulfuric acid before use. The solutions for modification contained 5–15 mM PDDA (Wako Pure Chemical, M_w 157 kDa by light scattering) and 10–35 wt% isopropanol in deionized water. In all cases, the molar ratio of ionic groups of PDDA to sulfonic groups of the membrane exceeded 1. For unmodified and modified membranes, we determined the membrane permeability (P) to vanadyl ions,^{8,13} through-plane proton conductivity (σ),¹⁸ equilibrium swelling degree (α) and ion-exchange capacity (IEC). The staining of the membranes in the Bradford reagent solution¹⁹ was also performed. For the details of the experiments, see Online Supplementary Materials.

Modification of Nafion membranes in aqueous isopropanol-free PDDA solutions led to a negligible decrease in the membrane permeability to vanadyl ions, from 6×10^{-6} to 5×10^{-6} cm² min⁻¹. The proton conductivity of the membranes after modification also practically did not change (0.06 S cm⁻¹), which is in good agreement with the reference data.¹³ On the contrary, an increase in the isopropanol content in the modification solutions caused a progressive decrease in the P value of the modified membranes (by more than three orders of magnitude at 30–35 wt%

isopropanol), accompanied by at most sixfold decrease in their proton conductivity (Figure 1). Note that the PDDA concentration in the modification solution and the [PDDA]/[SO₃⁻] ratio had no detectable effect on the properties of the modified membranes.

The extraordinary effect of isopropanol on vanadyl ion permeability of the resultant membranes could be attributed to the strong swelling of the Nafion membrane in isopropanol–water mixtures, well known from the literature.^{6,15,16,20} Indeed, a significant increase in the membrane swelling degree observed at an isopropanol content above 10–15% correlated with a sharp decrease in the *P* value (see Figure 1). It seems that the enhanced swelling of the membrane promotes the penetration of PDDA into the hydrophilic regions of Nafion, causing their effective screening.

It is reasonable to assume that the transport properties of the membrane are determined by the degree of modification depending, in its turn, on the modification conditions. Unfortunately, we failed to measure any decrease in the PDDA concentration in the surrounding solution after the modification in all cases. Likewise, the IEC values of the modified membranes (0.87–0.93 mmol g⁻¹) did not differ significantly from those of the unmodified membrane. Furthermore, the IR spectra of the pristine and modified Nafion membranes were identical. Thus, the results obtained using several methods indicated extremely low modification degrees, below the respective detection limits.

The binding of PDDA with Nafion during modification was qualitatively confirmed by the membranes staining with the Bradford reagent which was developed for staining proteins in gels after gel electrophoresis.¹⁹ The reagent contains a dye, Coomassie Brilliant Blue G250, which, upon binding with cationic amino groups, changes the brown color of the original Bradford reagent ($\lambda_{\text{max}} \sim 470$ nm) (Figure 2, curve 1) to blue ($\lambda_{\text{max}} \sim 585$ –610 nm). Incubation of unmodified Nafion membranes in the Bradford reagent resulted in a light brown to black staining of the membranes, with the color intensity gradually increasing with incubation time due to the solubilization of the dye into the membrane interior [Figures 3(a),(d)]. In contrast, PDDA-modified membranes turned blue upon short-term (1.5 min) incubation in the Bradford reagent due to the binding of the dye with PDDA amino groups [Figures 3(b),(c)].

Prolonged incubation of the modified specimens in the Bradford reagent revealed a significant difference between membranes modified in the absence [Figure 3(e)] and in the presence [Figure 3(f)] of isopropanol. In the first case, the membrane gradually changes color from blue to brownish upon staining for 5–15 min (photo not shown) and then progressively to black [see Figure 3(e)]. The maximum in the absorption spectrum shifts from 600 ± 20 nm (Figure 2, curve 2) to 490 nm (Figure 2, curve 3), with the spectrum approaching that of the

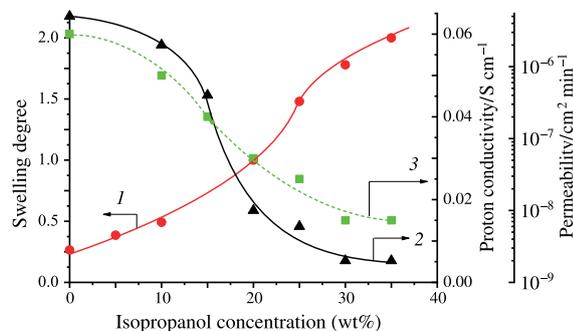


Figure 1 Effect of isopropanol concentration in modification solutions on (1) the swelling degree, (2) permeability to vanadyl ions and (3) through-plane proton conductivity of the PDDA-modified Nafion membranes. The initial concentration of PDDA was 15 mM, the duration of the modification was 24 h.

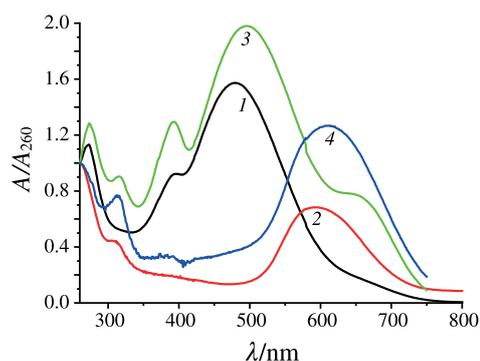


Figure 2 Normalized UV-VIS spectra of (1) the Bradford reagent solution and Bradford-stained Nafion membranes modified with PDDA in (2),(3) water or (4) aqueous isopropanol. The duration of staining with the Bradford reagent was (2) 1.5 min and (3),(4) 24 h.

Bradford reagent (see Figure 2, curve 1). An absorption maximum at 470 nm (475 nm in our case) was found for the cationic form of Coomassie Brilliant Blue G250 in a highly acidic environment.²¹ Many different factors, such as the dielectric constant of the environment, aggregation of the dye, Coulomb binding of the cationic groups of the dye with the sulfonate groups of Nafion and non-ionic interactions, can shift the spectral maxima. Taking this into account, we believe that the dye molecules penetrate the membrane transport channels coated with sulfonate groups of Nafion, providing a highly acidic environment. The similarity of the staining patterns obtained after a 24-h incubation of unmodified membranes and membranes modified in the absence of isopropanol demonstrates the availability of transport channels for large dye molecules in both cases and confirms that modification with PDDA in isopropanol-free aqueous solutions does not significantly change transport properties of the Nafion membrane.

On the contrary, the membranes modified with PDDA in the presence of isopropanol remained blue upon prolonged incubation in the Bradford reagent [see Figure 3(f)]. The persistence of the blue color upon prolonged staining indicates that modification in the presence of isopropanol leads to complete blocking of transport channels for large dye molecules, which correlates with a significant decrease in the permeability to vanadyl ions.

The stability of PDDA-modified membranes obtained in isopropanol-containing modification media was confirmed by unchanged transport properties after keeping the modified membranes in 2.5 M H₂SO₄ for a year, in contrast to unstable membranes modified in water.²²

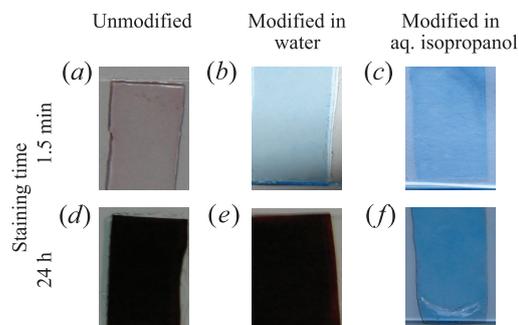


Figure 3 Typical photos of (a),(d) an unmodified Nafion 112 membrane and membranes modified with PDDA in (b),(e) water or (c),(f) aqueous isopropanol after staining with the Bradford reagent. Photos (b),(e) and (f) refer to spectra 2–4 in Figure 2, respectively.

In summary, the results obtained showed that the addition of isopropanol to the modification solutions caused a significant decrease in the permeability to vanadyl ions (up to 3.5 orders of magnitude), despite a very low degree of modification, while the decrease in proton conductivity was less pronounced (no more than six times). It should be noted that the decrease in membrane permeability correlated with the degree of its swelling during modification. We believe that, in the presence of isopropanol, PDDA molecules penetrate the transport channels of the swollen membrane, and the compaction of PDDA coils upon a decrease in the dielectric constant of the solvent promotes incorporation. The assumption about the penetration of PDDA chains into a highly swollen membrane is based on the following reasons: a significant decrease in the vanadyl ion permeation, accompanied by a complete rejection of dye permeability, and the high stability of the modified membranes in a 2.5 M H₂SO₄ solution, which radically distinguish them from the membranes with an easily removable surface polyelectrolyte layer applied from aqueous solutions, which does not notably change the permeation of vanadyl ions and the dye. Moreover, a negligible degree of modification and a relatively small decrease in proton conductivity indicate the penetration of PDDA into the mouth of the channel, and not through the entire membrane, in contrast to the equimolar modification of the Nafion membrane with a cationic surfactant, resulting in a decrease in proton conductivity by two orders of magnitude.⁸ The rapid collapse of the membrane when replacing the mixed solvent with water after modification can provide additional strong fixation of PDDA molecules within the mouths of the membrane channels and contribute to the stability of the membrane. Further experiments confirming and refining the proposed mechanism will be reported elsewhere.

Hence, introducing isopropanol as the co-solvent providing enhanced membrane swelling in the modification medium is a new, quite simple and promising approach to membrane modification, resulting in substantial improvement in the selectivity of Nafion membranes due to the significant decrease in the permeability to vanadyl ions.

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Online Supplementary materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.023.

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