

Perfluorinated sulfocation-exchange membranes modified with zirconia for sensors susceptible to organic anions in multiionic aqueous solutions

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Potentiometric sensors whose analytical signal is the Donnan potential can be developed for the determination of organic and sulfur-containing anions in multiionic aqueous solutions based on perfluorinated sulfonated cation-exchange membranes modified with zirconia.

Hybrid materials based on ion-exchange membranes and inorganic compounds are of interest in analytical chemistry.^{1–4}

Recently, we suggested the use of potentiometric sensors, whose analytical signal is the Donnan potential (PD-sensors) for the determination of bioactive substances in multiionic solutions.⁵

The aim of this work was to investigate the applicability of perfluorinated sulfocation-exchange polymeric (PSP) membranes doped with zirconia as the electrode-active materials of potentiometric sensors for organic anions in multiionic aqueous solutions. The PSP membranes doped with zirconia were obtained as described elsewhere.⁶

The individual aqueous solutions of HCl, HNO₃, KCl and KGly (equimolar solutions of KOH and glycine with pH from 6.54±0.05 to 11.61±0.05) were investigated for estimating the influence of counter- and co-ions on the response of PD-sensors. The aqueous solutions of cysteine (Cys) and KOH were used for evaluating the possibility of organic and sulfur-containing anions determination in multiionic aqueous solutions by PSP-based PD-sensors. Such solutions contained an excess of KOH (pH from 9.71±0.05 to 13.55±0.05), the anions MeCOCOO⁻, HS⁻ and OH⁻ and the cations K⁺, NH₄⁺ in concentrations 1.0×10⁻⁴–5.0×10⁻² mol dm⁻³.

Transmission electron microscopy (TEM) has shown nanoparticles formation in a membrane matrix with a size of 2–7 nm (Figure 1). ZrO₂ incorporation into PSP results in an increase in ion conductivity in comparison with unmodified PSP. The highest ion conductivity was observed for the PSP modified with 5 wt% ZrO₂. The conductivity was 6.5×10⁻² Ω⁻¹ cm⁻¹ at 25 °C that is 0.5 order of magnitude higher than that of the initial PSP. Moreover, the PSP modification leads to a decrease in the con-

Table 1 Diffusion permeability coefficients (cm² s⁻¹) of PSP membranes obtained by casting method.

Diffusing solution	MF-4SC membrane	MF-4SC + 5 wt% ZrO ₂	MF-4SC + 7 wt% ZrO ₂
0.1 NaCl	(7.00±0.05)×10 ⁻⁸	(5.14±0.04)×10 ⁻⁸	(9.41±0.05)×10 ⁻⁹
0.1 HCl	(2.39±0.02)×10 ⁻⁷	(4.50±0.04)×10 ⁻⁷	(1.26±0.02)×10 ⁻⁷

ductivity activation energy from 13.7±0.2 kJ mol⁻¹ for unmodified PSP to 10–12 kJ mol⁻¹ for modified membranes.

The diffusion coefficients of PSP membranes doped with 5 and 7 wt% ZrO₂ in 0.1 M NaCl solution are (5.14±0.05)×10⁻⁸ and (9.41±0.04)×10⁻⁹ cm² s⁻¹, respectively, which are lower than that for the initial PSP membrane [(7.00±0.05)×10⁻⁸ cm² s⁻¹] (Table 1). The cation diffusion rate is higher than the anion diffusion rate in the PSP membranes. Thus, diffusion permeability is limited by the anion diffusion rate. Therefore, zirconia incorporation results in a considerable selectivity increase.

Analysis of characteristics of PD-sensors in HCl, HNO₃, KCl and KGly test solutions revealed a significant influence of counterions on the sensor response for all PSP samples, which is changed in accordance with the degree of counter-ions hydration. The most considerable effect of co-ions on the analytical signal of PD-sensors was observed for K⁺-type PSP samples one side of which was modified with zirconia (5 wt%) while another side was initial PSP. For these PSP samples, the increase in response and sensitivity values was 11±5 mV and 8±4 mV (pC)⁻¹, respectively, in KCl test solutions in comparison with KGly test solutions. These samples were chosen for the organisation of a PD-sensor to detect organic anions in multiionic test solution.

Calibration equations of gradient modified PSP-based PD-sensor in solutions, containing MeCOCOO⁻, HS⁻, OH⁻, K⁺ and NH₄⁺ were compared with calibration equations of extrusion unmodified PSP-based membrane (no. 4) in similar solutions. The following calibration equation was used:

$$\Delta w_D = b_0 + b_1 pC_+ + b_2 pC_- + b_3 pH, \quad (1)$$

where Δw_D is the analytical signal of PD-sensor (mV); C_+ is the total concentration of the cations K⁺ and NH₄⁺ (mol dm⁻³); C_- is the total concentration of the anions MeCOCOO⁻ and HS⁻ (mol dm⁻³); b_0 is a free term (mV); b_1 is the sensitivity of the sensor to cations, b_2 is the sensitivity of the sensor to anions, and b_3 is the sensitivity of the sensor to hydroxonium ions [mV (pC)⁻¹].

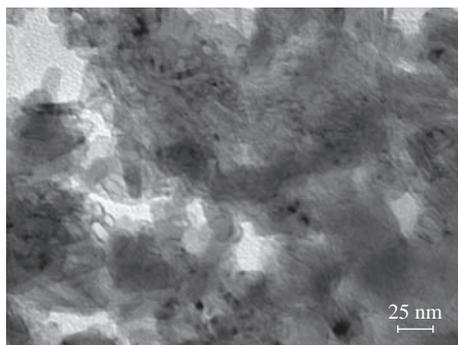


Figure 1 TEM data for MF-4SC membrane doped with 5 wt% ZrO₂.

Table 2 Coefficients of calibration equations (1) of PSP-based PD-sensors in aqueous solutions containing MeCOCOO⁻, HS⁻, OH⁻, K⁺ and NH₄⁺ ions.

Coefficient	Unmodified PSP membrane	PSP membrane doped with ZrO ₂ (gradient distribution)
$b_0 \pm \Delta b_0 / \text{mV}$	-4±2	-12±2
$b_1 \pm \Delta b_1 / \text{mV (pC)}^{-1}$	-48±1	-48±1
$b_2 \pm \Delta b_2 / \text{mV (pC)}^{-1}$	0.0±0.8	2.5±0.8
$b_3 \pm \Delta b_3 / \text{mV (pH)}^{-1}$	-5±1	-2±1

It was shown (Table 2) that the use of PSP membrane with gradient ZrO₂ distribution for PD-sensor leads to significant contribution of anions into the analytical signal in contrast to unmodified PSP samples. The difference between sensor responses calculated by equation (1) and experimental sensor responses in aqueous solutions containing MeCOCOO⁻, HS⁻, OH⁻, K⁺ and NH₄⁺ ions at pH 9.7–13.6 is 3%.

Since ZrO₂ particles in modified membranes give evidence of both cation- and anion-exchange properties,⁷ co-ions concentration near modified PSP/test solution of electrolyte interface increases compared to unmodified PSP. This allows us to increase the sensitivity of gradient modified PSP-based PD-sensors to co-ions in aqueous solutions. The effect of co-ions on the response of uniform distribution modified PSP-based PD-sensors is insignificant due to the fact that co-ions concentration gradients on the PSP/test solution and PSP/reference solution interfaces are oppositely directed and compensate each other.

The results evidence the possibility of using modified K⁺-type PSP samples with gradient on the length ZrO₂ distribution

as electrodoactive material in PD-sensors, which are sensitive to organic anions in aqueous solutions. Such PD-sensors with ion-selective electrodes can be promising for the determination of organic and sulfur-containing anions in multiionic aqueous solutions.

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