

IONIC CONDUCTIVITY OF GRANULATED ORGANIC-INORGANIC ION-EXCHANGERS

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A number of organic-inorganic granulated materials based on Dowex SBR-P and Dowex HCR-S ion exchange resins were synthesized. The resins were modified with nanoparticles of hydrated oxides of Zr(IV), Ti(IV), Sn(IV) or Fe(III). Specific electrical conductivity of the polymer and composite ion-exchangers were measured. The materials were equilibrated preliminarily in deionized water. The method of impedance spectroscopy was applied to measurements. Nyquist and Bode plots were used for determination of conductivity. The most adequate equivalent schemes were found. Unlike other inorganic constituents, hydrated tin dioxide increases the conductivity of the Dowex SBR-P anion-exchange resin. The conductivity of Dowex HCR-S cation exchanger increases 3-5 fold after precipitation of all mentioned modifiers. Thus, hydrated tin dioxide is the most suitable for modification of anion exchange membranes. All investigated oxide inorganic sorbents can be recommended for preparation of organic-inorganic cation exchange membranes.

Among the existing methods for removal of toxic or valuable ionic components from water, membrane filtration and sorption are the most effective techniques. In order to provide selective recovery of certain ions from diluted aqueous solutions by means of continuous gradient-controlled processes, membranes and sorption materials have to possess the following characteristics: high selectivity, significant electrical conductivity and reversibility of ion sorption. It is known that fast transport of counter-ions in highly hydrated inorganic compounds, such as hydrated oxides, is caused by a significant amount of water molecules on the particle surface [1]. These materials are also characterized by considerable selectivity towards toxic ionic species. On the assumption of optimal combination of high electrical conductivity and selectivity, hydrated oxides of Zr(IV), Ti(IV), Sn(IV), and Fe(III) were chosen as inorganic constituents for preparation of organic-inorganic ion-exchangers. The advantage of these materials over inorganic ion-exchangers is large granules, which provide low hydrodynamic

resistance of the bed, which is placed between the membranes. Moreover, the inorganic materials could be proposed for modification of membrane for electrodialysis. The modification provides higher permittivity towards counter-ions, on the one hand, and stability of the membranes against fouling with organics, on the other hand.

Research Methodology

Dowex SBR-P strongly basic anion exchange resin and Dowex HCR-S strongly acidic cation-exchanger (produced by Dow Chemical) were chosen for investigations. The organic-inorganic granulated ion-exchangers were synthesized by impregnation of the polymer matrix with a solution of salt of corresponding metal. The inorganic constituent was precipitated inside granules of the polymer ion-exchanger with a NH_4OH solution [2]. Electrical resistance of the ion-exchange granules was measured in a cell of a capacitor type supplied with platinized titanium electrodes. Impedance spectra were measured within the frequency diapason of 10^{-2} - 10^6 Hz. Preliminarily the ion-exchangers were immersed into deionized water for swelling. A PGSTAT 302N Metrohm Autolab electrochemical module was applied to measurements. The specific conductivity was calculated from the plateau of impedance spectra (which corresponds to dc conductivity) taking into consideration the cell constant (m^{-1}). Another way was to find the most suitable equivalent scheme.

Results and Discussion

The Nyquist and Bode plots for the cation exchange composites containing SnO_2 (28%) or ZrO_2 (22%) are depicted in Fig. 1. The values of active resistance obtained by Nyquist plot extrapolation, are 350 and 520 Ohm respectively. The values of specific conductivity obtained by calculation are relatively high (0.27 and $0.23 \text{ Sm}\cdot\text{m}^{-1}$) and much higher in comparison with data for the pristine resin ($0.08 \text{ Sm}\cdot\text{m}^{-1}$).

In the case of cation exchanger, the charge carriers are assumed to be hydroxonium ions H_3O^+ . The obtained value allows us to suppose high mobility for adsorbed cations as well as reversibility of their sorption. The data also show a possibility of using the organic-inorganic ion-exchangers for the process, which combines electrodialysis and ion exchange and is directed to removal of certain ions from diluted solutions.

The conductivity values for the composite ion-exchangers are plotted in Fig. 2 as functions of amount of incorporated inorganic constituent. As shown, the particles of hydrated tin dioxide increase the ionic conductivity of the Dowex SBR-P anion-exchanger. The growth is 2-fold. Other inorganic ion-exchangers reduce the conductivity. At the same time, the conductivity of the Dowex HCR-S cation-exchanger

increases 3-5 fold after modification with hydrated oxides of Zr(IV), Ti(IV), Sn(IV) and Fe(III).

The obtained data can be explained as follows. Regarding the two-phase system, as the volume fraction of the conducting phase increases, the resulting conductivity of the composite obeys a percolation model [3, 4]. In accordance with this model, the resulting conductivity is determined by the amount and conductivity of more conducting constituent, when these parameters achieve certain values (percolation threshold).

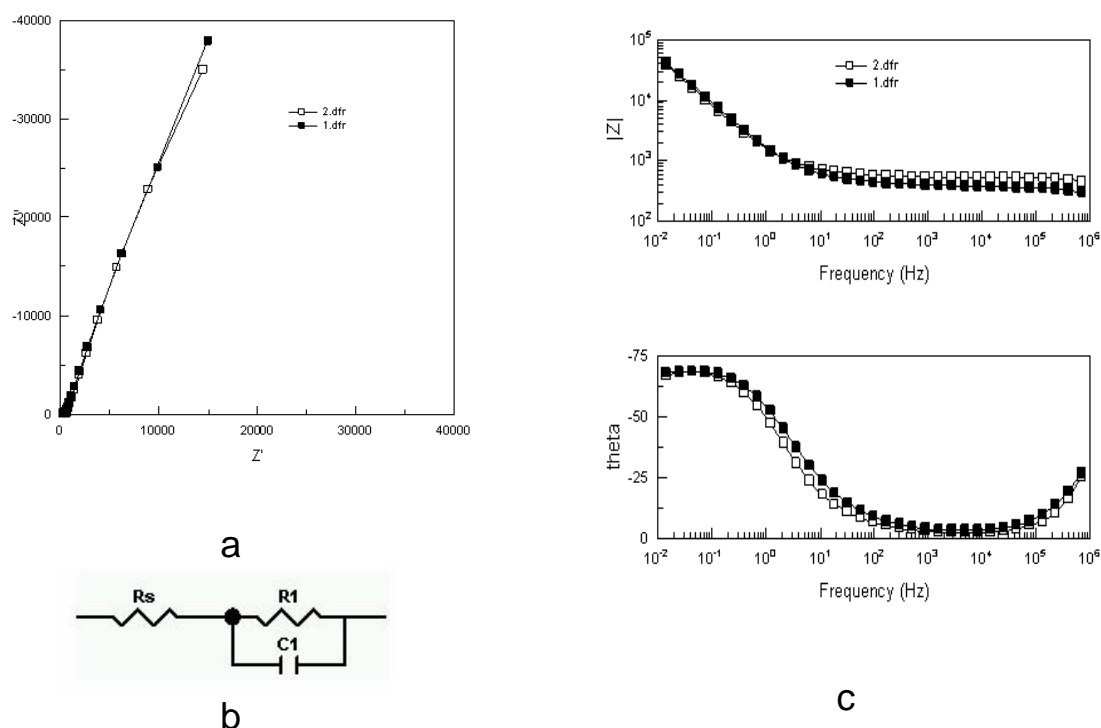


Fig. 1. Nyquist plot (a), equivalent scheme (b) and Bode plots (c) for cation-exchangers containing SnO₂ (1) and ZrO₂ (2). Here R_s are the bulk resistance, R_1 is the resistance of the solid-liquid interface, C_1 is its capacity.

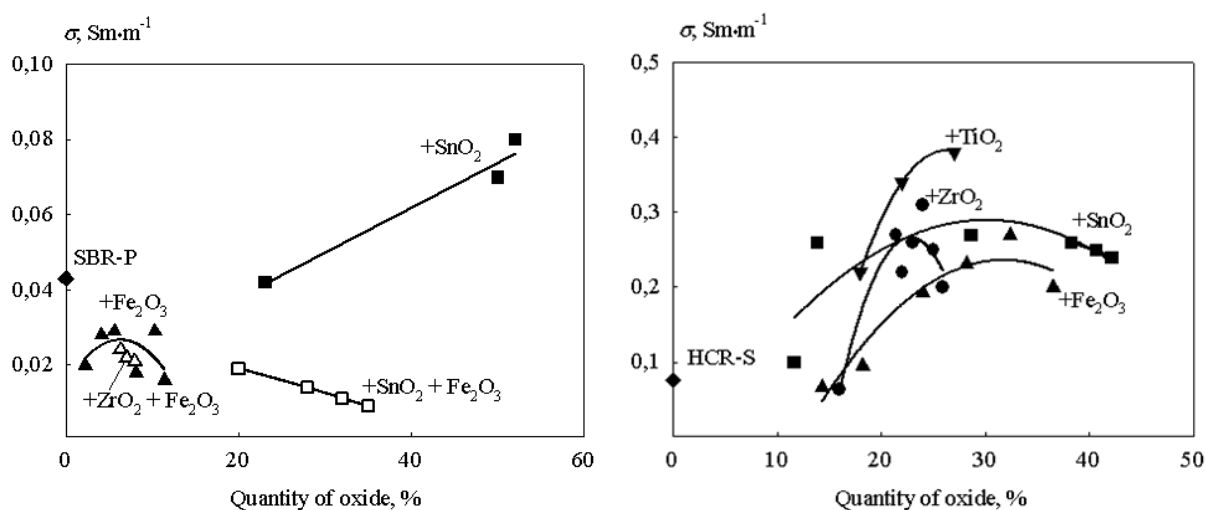


Fig. 2. Specific conductivity of composite ion-exchangers as a function of amount of incorporated hydrated oxide.

The main charge carriers in the composite anion-exchangers should be hydroxyl-ions. Probably, no percolation threshold is reached for the composite anion-exchangers due to insufficient concentration of OH⁻ ions.

Conclusions

Electrical conductivity of the composite cation-exchangers in deionized water is relatively high and much higher in comparison with the pristine resin. The conductivity of Dowex HCR-S polymer cation-exchangers containing particles of hydrated oxides of Zr(IV), Ti(IV), Sn(IV) increases 3-5 fold in comparison with the pristine resin. The obtained values allow us to suppose high mobility of sorbed ions and reversibility for sorption processes. The data confirm the perspective usage of the inorganic ion-exchangers for modification of cation exchange membranes to provide their high permittivity towards counter-ions and stability against fouling with organics.

The main charge carriers in composite cation- and anion-exchangers are protons and hydroxyl-ions, respectively. In accordance to the percolation model, the conductivity of two-phase system is determined by the amount and conductivity of the more conducting component if these parameters achieve certain values. In the case of the composite anion-exchanger, the percolation threshold is not reached. However, the threshold is reached for the composite containing hydrated tin oxide. This inorganic ion-exchanger could be used further for modification of anion exchange membranes.

References

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