



Selectivity of Transport Processes in Ion-Exchange Membranes: Relationship with the Structure and Methods for Its Improvement

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Abstract

Nowadays, ion-exchange membranes have numerous applications in water desalination, electrolysis, chemistry, food, health, energy, environment and other fields. All of these applications require high selectivity of ion transfer, i.e., high membrane permselectivity. The transport properties of ion-exchange membranes are determined by their structure, composition and preparation method. For various applications, the selectivity of transfer processes can be characterized by different parameters, for example, by the transport number of counterions (permselectivity in electrodialysis) or by the ratio of ionic conductivity to the permeability of some gases (crossover in fuel cells). However, in most cases there is a correlation: the higher the flux density of the target component through the membrane, the lower the selectivity of the process. This correlation has two aspects: first, it follows from the membrane material properties, often expressed as the trade-off between membrane permeability and permselectivity; and, second, it is due to the concentration polarization phenomenon, which increases with an increase in the applied driving force. In this review, both aspects are considered. Recent research and progress in the membrane selectivity improvement, mainly including a number of approaches as crosslinking, nanoparticle doping, surface modification, and the use of special synthetic methods (e.g., synthesis of grafted membranes or membranes with a fairly rigid three-dimensional matrix) are summarized. These approaches are promising for the ion-exchange membranes synthesis for electrodialysis, alternative energy, and the valuable component extraction from natural or waste-water. Perspectives on future development in this research field are also discussed.

Keywords: ion-exchange membranes; functional polymers; selectivity; ionic conductivity; hybrid membranes; grafted membranes

Introduction

Ion exchange membranes (IEMs) are actively used in modern technologies, including water purification, concentration, electrochemical synthesis, and sensors. Their use in fuel cells, in energy storage and conversion systems, e.g., metal-ion batteries, reverse electrodialysis, and redox batteries has received the most attention in recent years. There are a number of other technologies in which ion-exchange membranes can also be used. For example, they can successfully compete with porous membranes in the processes of alkenes/alkanes separation. Undoubtedly, ionic conductivity plays a dominant role in these applications. Even the above-mentioned alkene transfer proceeds via the a complex with silver ions or protons. At the same time, the ion separation by membranes never occurs with 100% selectivity and is usually accompanied by an undesired transfer of molecules or opposite charged ions. Despite the fact that these processes proceed to a much less extent, they usually determine the decrease in the efficiency of electrodialysis, fuel cells and other devices based on ion-exchange membranes. That is why their understanding is so important for numerous membrane technologies.

The Ion Exchange Membrane Structure and Ion Transfer

Description of the ion-exchange membrane structure should be started from one of the benchmark materials—perfluorosulfonic acid membranes of the Nafion type. Nafion is a random copolymer of

tetrafluoroethylene and sulfonyl fluoride vinyl ether. The first of them forms a hydrophobic perfluorinated backbone, and the second forms a side chain with $-SO_3H$ ($-SO_3M$) terminal group. The latter are hydrophilic and, as result of self-organization, form clusters, which absorb water from the environment. As a result, there is an extended network of pores (4–5 nm in size in a swollen state) and channels filled with water in the membrane. Dissociation of functional groups leads to the formation of an aqueous solution containing dissociated cations.

Pseudo-Homogeneous and Grafted Membranes

The obvious desire is to create relatively cheap membranes, for example, similar in composition to heterogeneous ones, but with high selectivity like in homogeneous membranes, primarily perfluorinated sulfonic acid membranes. To do this, one should get rid of the macropores formed during the heterogeneous membrane preparation. The most evident approach seems to prepare homogeneous membranes based on sulfonated polystyrene (PS), which is the basic ion-exchange material for the preparation of most of heterogeneous membranes. However, it is impossible to obtain films with good mechanical properties from it. That is why a binder, most often polyethylene, is used to form heterogeneous ion-exchange membranes.

Cross-Linking of Polymer Membranes

It can be assumed that there is a certain optimal size of pores and channels connecting them to ensure a good combination of ionic conductivity and selectivity of ion-exchange membranes. On the one hand, to provide high ionic conductivity of the membranes, large channels and pores are required, and hence a high water uptake. However, if we refer to the example with grafted membranes, the fact that membranes with intermediate water uptake have optimal transport properties can be seen. At low water uptake, the whole pore/pore volume is covered by a double electric layer and the coion concentration in them is negligible.

Conclusions

The above material indicates that the transport properties of ion-exchange membranes are determined primarily by their structure, which in its turn depends on the membrane preparation method. As shown in a number of publications, there is a trade-off between the membrane permeability/conductivity and the selectivity of the transfer rate of the target component. In this regard, the quality of membrane material can be characterized by means of the relation between the permeability and permselectivity, for example, by the relation between the ionic conductivity and counterion transport number (in electrodialysis) or ionic conductivity and permeability of fuel molecules (crossover in fuel cells). To enhance this relation, a wide range of approaches is used, such as crosslinking, preparation of hybrid membranes with embedded nanoparticles, and surface modification.

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