Characterization of nanoporous active layers of composite ceramic membranes via time-resolved electrical measurements

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Abstract

Surface-charge density is widely recognized as an important property of nanoporous membranes controlling transmembrane transport of ions (cf. Donnan exclusion) as well as electrostatic interactions with charged macromolecules important for membrane-fouling control. This property can be estimated from ion perm-selectivity. Moreover, the knowledge of the latter can be useful for understanding trans-membrane ion transfer even regardless of its relationship with the surface-charge density. Ion perm-selectivity, in principle, can be determined from stationary membrane potential (electric-potential difference induced by an applied salt-concentration difference at zero electric current). However, in the case of composite membranes (especially, ceramic ones having generally thick support layers), the interpretation of measurements of stationary membrane potential is complicated by the typically dominant contribution of support layers to the diffusion resistance. As a result, only a small (and often poorly known) part of the applied concentration difference is located on the membrane active layer.

Another popular method for obtaining information on the surface charge is the so-called filtration potential, which is an electrical response to an applied hydrostatic-pressure difference. Here again relatively thick support layers of composite ceramic membranes give rise to problems because they often make a dominant contribution to the measured electric-potential difference. In addition, in the case of nanoporous active layers, this contribution non-linearly depends on the applied pressure, which complicate its subtraction and obtaining information on the active-layer properties [1].

To address these issues, we developed (and applied to composite ceramic membranes) two non-stationary techniques for the measurements of transient electrical response. In the **pressure switch-off technique**, a constant pressure difference is applied until steady filtration state is reached. In stationary nanofiltration, there are no salt-concentration gradients in support layers, so the whole concentration difference is located on the active layer (provided that external concentration polarization is eliminated via vigorous feed stirring). This concentration difference can be determined from measurable salt rejection. When the pressure difference is suddenly switched off, the salt-concentration difference initially remains located on the active layer while streaming-potential component vanishes synchronously with the pressure difference. From the potential difference measured immediately after the pressure switch-off and the steady-state salt rejection, one can determine ion perm-selectivity. However, this initial state can relax very quickly, so to be able to determine it, the pressure difference has to be switched off very rapidly. Extrapolation to very short times using a theoretical model is also essential.

We have developed a semi-batch NF setup where applied pressure can be switched off from as much as 25 bar down to zero in less than 50-100 ms [2]. This setup was used to study a laboratory-made nanoporous ceramic membrane (α-alumina-supported γ-alumina, average pore size 4 nm). Fig.1 shows examples of time transients obtained for various pressures in 30 mM KCl solution and two-parameter theoretical fits (dashed lines). The agreement with a simple model is very good (for times > 100 ms). Even though strictly initial values could not be directly measured, the model made possible reliable extrapolation to very short times and determination of ion perm-selectivity from the extrapolated values and separately measured salt rejections. Simultaneous availability of information on ion perm-selectivity and salt rejection made possible evaluation of contributions of Donnan and non-Donnan mechanisms to the salt rejection by this nanoporous ceramic membrane.
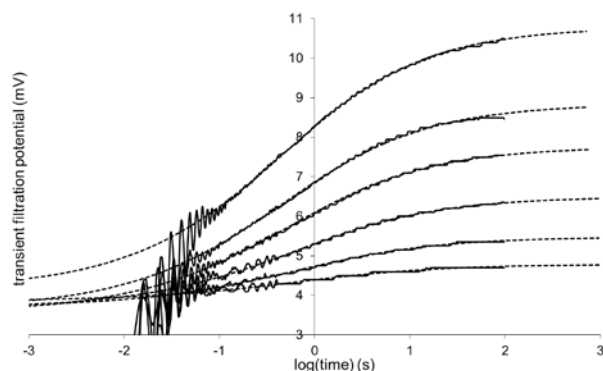
Fig.1. Time transients of filtration potential measured after pressure switch-off with a composite nanoporous ceramic membrane: $\Delta P = 0.3; 0.6; 1.0; 1.5; 2.0; 2.5 \; MPa$ (from bottom to top)

In another technique (**concentration step**) [3,4], a composite membrane is equilibrated with an electrolyte solution and is left in contact with this solution from the support side only. The active membrane side is touched by a droplet of the same solution having a different concentration and electrical response to this is measured.
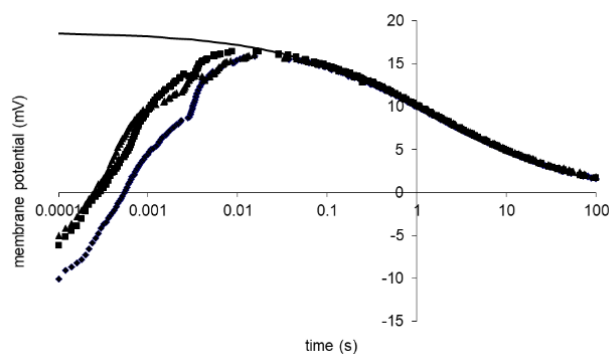

Fig.2. Transient membrane potential after concentration step measured with a composite nanoporous ceramic membrane: 0.03 M KCl (equilibrium)/0.01 M KCl (non-equilibrium)

Fig.2 shows the results of three repeated concentrated-step measurements performed with the same ceramic membrane as used in the pressure switch-off measurements. At longer times (>30 ms), the reproducibility is excellent. From the theoretical fit (solid line) one could estimate the anion perm-selectivity of 0.86 (positive fixed charge). The "overshooting" to the negative values at short times may be explained by the existence of a thin negatively charged fouling layer on top of the positively charged active layer. Remarkably, the presence of such hypothetical layer did not affect hydraulic permeability or salt rejection. Therefore, this measurement can be useful for early detection of fouling.

References

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