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Characterization of hollow fiber membranes by impedance spectroscopy

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ABSTRACT

Electrical impedance spectroscopy (EIS) is a simple and non-destructive method to characterize membranes and to monitor membrane processes. It can be used for instance to determine layer thicknesses or to observe fouling. Up to now it has only been applied to flat sheet membranes using a four-electrode measuring technique. Hollow fiber membranes are finding increasing application but monitoring the state of such membranes during operation is a difficult task. The aim of our work presented here is to adapt the electrical impedance spectroscopy method for use with hollow fiber membranes.

For this purpose a new membrane module has been developed which allows electrical impedance measurements to be made on hollow fibers and capillary membranes using a 2-terminal method. For this one wire-shaped electrode is located inside the hollow fiber membrane and one ring-shaped electrode is located outside, around the membrane. In the experiments the applied AC field used in the impedance measurements was in a radial direction; across the membrane from the lumen side to the shell side while the system was bathed by an electrolyte solution. A porous hydrophobic PP membrane with a pore size of 0.2 μm has been intensively analyzed with the new device to explore the characteristics of the new methodology.

The impedance of the ionic double layers and the frequency dependence of those impedances, at the two electrodes used in these experiments pose a major problem. These complications can normally be avoided by the use of 4-terminal methods but this is even more intricate to do with the hollow fiber geometry due to lack of space. Nevertheless, using the 2-terminal technique, it was possible to obtain meaningful impedance spectra. The membrane's impedance could be determined and a significant influence of the membrane wetting could be observed. Such wetting phenomena are often speculated about when analyzing flux data, but can now be quantified systematically. Furthermore, we present a comprehensive model to illustrate the opportunities and challenges for the developed technique.

1. Introduction

Electrical impedance spectroscopy (EIS) can be used as a simple non-destructive and non-invasive method to characterize membranes and monitor membrane processes [1]. The electrical impedance (EI) is the complex electrical resistance that is defined by the ratio of an alternating voltage to its corresponding current as well as the phase difference between them [2,3]. The range of applications of EIS in membrane science is far-reaching.

Electrical characteristics of membranes that can directly be determined by EI measurements are the electrical conductance, capacitance and inductance. Beyond that different layers can be distinguished and physical properties can be derived out of EI spectra indirectly by creating models in the form of equivalent circuits [4]. Physical properties that can be derived by those models are e.g. the porosities and the thicknesses of different membrane layers [5–7]. Not only the structure and the properties of the membrane itself but also the resistances at interfaces between the electrolyte and the electrodes [8–13] or the membranes [14,15] have been investigated intensively by EIS. Furthermore EIS have been used to monitor membrane processes by observing the fouling [16–23].

However, almost all the membrane research using EIS has been performed on flat-sheet membranes. To the author's best knowledge hollow-fiber, tubular and capillary membranes have barely been investigated so far. This is in fact surprising considering the huge amount of applications of hollow-fibers especially in industry and commercial usage. Only some research investigating

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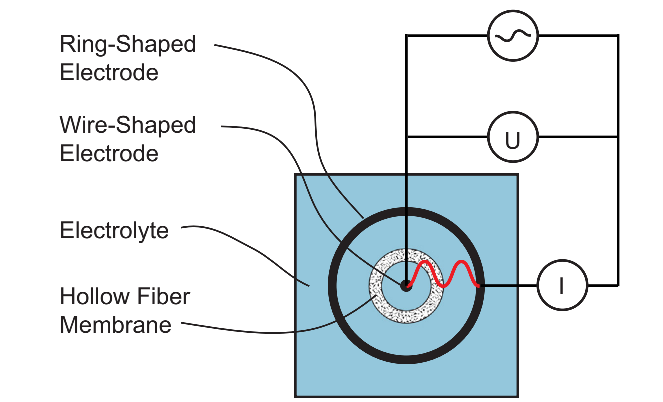

Fig. 1. Cross-sectional visualization of the principle of measurement for the analysis of hollow fibers: a ring shaped electrode encircles the hollow fiber on the shell side while a wire shaped electrode is put through the lumen side. The impedance can then be measured in a 2 electrode method in a radial electric field.

the conductive behavior of the membrane body of conducting cylindrical membranes has been performed so far [18,19,24,25]. But work analyzing the structure of non-conducting cylindrical membranes, the interface at cylindrical membranes or the fouling by EIS has not been reported so far in literature.

Developing a method to characterize even non-conducting cylindrical membranes by EIS could open up the broad range of applications that have been demonstrated with flat-sheet membranes to cylindrical membranes.

Here we present the first concept of a device design for the characterization of hollow-fiber membranes by impedance spectroscopy. The principle of the measurement is depicted in Fig. 1.

The concept involves the use of a two-electrode technique in contrast to a four-electrode technique that is usually used with flat sheet membranes. The four-terminal technique includes two additional reference electrodes to measure the potential developed across the membrane. [26]. In the current two terminal device a wire-shaped electrode is positioned inside the lumen side of the membrane and a ring shaped electrode encircles the membrane on the outside. The whole system is immersed in an electrolyte solution. Thereby the impedances can be measured by applying an AC field in radial direction between those two electrodes at a range of frequencies. The lack of space inside the lumen side of the membrane prevents the implementation of the four terminal technique which involves the additional reference electrodes. Using a two-electrode technique has the consequence that the impedance of the ionic double layer at the electrode–electrolyte interface is measured in addition to that of the membrane and thus must be considered during data analysis. In this work we show how in general EIS can be adopted for the characterization of hollow-fiber membranes and what challenges have to be faced thereby. Giving the theoretical background we point out how the impedances can be modeled in a radial field. Commercial hollow-fibers were investigated as a first proof of concept. Thus this work is the first step for the adaption of the broad range of application opportunities of EIS for hollow fiber membranes.

2. Theoretical background

Electrical impedance spectroscopy (EIS) is a versatile technique for membrane characterization. Although its application-fields are far reaching the measuring principle is intriguingly simple. The EI can be calculated in accordance to Ohm's law as

$$Z = \frac{U_{(t)}}{I_{(t)}} \tag{1}$$

wherein Z is the impedance, $U_{(t)}$ the voltage and $I_{(t)}$ the current. If an alternating voltage (A.C. voltage) is applied then – in contrast to direct current (DC) – $U_{(t)}$ and $I_{(t)}$ are functions of time (t). The A.C. voltage can be described as a complex number

$$U_{(t)} = \hat{U}_{(\omega)} \cdot (\cos(\omega t) + j \cdot \sin(\omega t)) = \hat{U}_{(\omega)} \cdot e^{j(\omega t)} \tag{2}$$

wherein $\hat{U}_{(\omega)}$ is the amplitude of the voltage's sine wave with an angular frequency ω and j the imaginary unit ($\sqrt{-1}$).

The resulting current can correspondingly expressed as

$$I_{(t)} = \hat{I}_{(\omega)} \cdot (\cos(\omega t + \varphi) + j \cdot \sin(\omega t + \varphi)) = \hat{I}_{(\omega)} \cdot e^{j(\omega t + \varphi)} \tag{3}$$

wherein $\hat{I}_{(\omega)}$ is the amplitude of the current´s sine wave and φ the phase shift between $U_{(t)}$ and $I_{(t)}$.

Inserting Eqs. (2) and (3) into Eq. (1) yields to the fundamental correlation that is used to determine the impedance in EIS

$$Z = \frac{\hat{U}_{(\omega)} \cdot e^{j(\omega t)}}{\hat{I}_{(\omega)} \cdot e^{j(\omega t + \varphi)}} = \underbrace{\frac{\hat{U}_{(\omega)}}{\hat{I}_{(\omega)}}}_{\hat{Z}_{(\omega)}} e^{-j\varphi} = \underbrace{\hat{Z}_{(\omega)} \cdot \cos(\varphi)}_{real\ part} - \underbrace{j \cdot \hat{Z}_{(\omega)} \cdot \sin(\varphi)}_{imaginary\ part} = Z_{(\omega)} \tag{4}$$

The impedance $Z_{(\omega)}$ can hence be obtained directly for each frequency ω by measuring $\hat{U}$, $\hat{I}$ and φ.

Impedance data measured at a range of frequencies can subsequently be used to derive physical and structural properties by using an equivalent circuit model. Such a model can be build up by combining a number of different equivalent circuit elements in parallel or in series. The model then can be fitted to the measurement data obtained by Eq. (4).

Two standard equivalent circuit elements are predominantly used in these models. The first one is the frequency-independent Ohm's resistance R who's impedance can described as

$$Z_R = R \tag{5}$$

This is usually used to describe any electrical conductance that is not dependent on the frequency. It should be noted that R is an integral area specific value that can be determined by the following equation:

$$R = \frac{1}{\sigma} \int_{x_1}^{x_2} \frac{1}{A} dx \tag{6}$$

wherein σ is the electric conductivity of the observed material or medium, x the pathway of the current and A the cross-section area through which the current is flowing. In parallel electrode arrangements with planar electrodes axis usual for flat sheet membranes the cross-sectional area is constant over the pathway. However, for radial electrode arrangements like it is used in this work the cross-section area is changing along the pathway. Therefore a correlation must be found to describe the dependence of A on x. A detailed derivation of the model for the cylindrical geometry of the device that is presented in this work is given in Appendix A of this manuscript.

The second equivalent circuit element is an ideal capacitor. A capacitor's impedance is frequency dependent and can be expressed by the following equation:

$$Z_c = \frac{1}{j\omega C} \tag{7}$$

wherein C is the capacitance. The imaginary unit j indicates that there is a phase shift of $-(\pi/2)$ between the voltage and current. That means the voltage is lagging 90° behind the current.