Characterisation of membrane materials by means of electrochemical impedance spectroscopy

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Abstract

The characterisation of membranes (or porous media) is usually effected with absorption or optic techniques. In most cases these techniques are cumbersome and require expensive equipment. The impedance spectrum obtained with a membrane interposed between two electrodes yielded substantial information on the character (hydrophilic/hydrophobic) of the membrane and could be used to distinguish between the two types of membranes. This is of importance for example in the affinity of solvent extractants for the membrane where these are used in SLM studies. The inherent characteristics of a membrane, such as its permeability and tendency for polarisation, are important for design purposes where transmembrane transport is concerned.

Introduction

Selection of a membrane material for reverse osmosis, ultrafiltration or hydrometallurgical transport processes has been done over recent years from the data obtained by direct and alternating current measurements. Pressure gradient measurements in addition lead to characterisation of such membranes. A determination of the different elements, i.e. the skin and sublayers of membranes, is difficult as it is not easy to separate the components of the membrane using all the aforementioned techniques.

Most of the current interest in modelling of membranes is in the field of reverse osmosis and ultrafiltration, and relatively little work has been forthcoming in the hydrometallurgical application of supported liquid membranes.

Electrochemical impedance spectroscopy (EIS) techniques, developed over the last 20 years, have largely concentrated on the study of corrosion and only little work has been done on ultra-filtration and reverse osmosis membranes or membranes in general. This paper focuses on the Celgard membrane series which are constructed in a different manner from the anisotropic membranes for reverse osmosis.

An interesting observation from EIS measurements on Celanese products was the grouping of data into two distinct categories. As might be anticipated, hydrophobic and hydrophilic membranes behaved quite differently when probed by the EIS technique. A further observation was that reverse osmosis membranes measured by other workers yielded data which fitted into one or other category of hydrophobic-like or non-hydrophobic membranes (i.e. hydrophilic) when studies in inorganic salt solutions were undertaken.

In order to select the optimum membrane for metal cation transport where the membrane is impregnated with an insoluble organic extractant, the transport properties of the membranes in salt solutions alone need to be investigated.

The present study looks at the characterisation of two membranes types in the presence of simple salt solutions (e.g. KCl). This was done to simplify the interpretation of results and as a preliminary study to a real transport situation. Only dilute solutions of KCl were investigated in an effort to study the electrical double layer of the membrane/aqueous interface.

Many studies of membranes used in reverse osmosis are done with sulphate or sulphite solutions as these are most relevant to the industrial problems, whereas traditionally the KCl or KF interface has been used in the double-layer studies of the electrode/solution interface. Theoretical models of the metal/aqueous solution interface, already well established by other workers (Armstrong et al., 1984; Schumann et al., 1979; Erscher, 1947), were used to fit the experimental results and to calculate resistances and capacitances. The measured capacitance allows the calculation of the membrane porosity. This is to be elaborated on in another paper submitted for publication.

In addition to three-dimensional representation of the characterisation data with respect to time dependence of the spectra, new membrane products may now be grouped.

Experimental

For the impedance measurements the four-electrode system was used (which is fairly standard in electrochemical impedance spectroscopy). Silver/silver chloride electrodes of a commercial variety were used as reference electrodes and analytically pure KCl with deionised water was used to make up the electrolytes. Solartron 1255 frequency response analyser input into an EG&G PARC Model 273 potentiostat enabled the frequency of a small alternating current to be varied between 10^{-1} and 10^5 Hz. A signal with a maximum amplitude of 10mV was the value used in all the experiments presented in this paper. Control of the system by an IBM PS/2 Model 70 computer allowed the calculation of resistances and capacitances from a computer-fitted curve or alternatively a Bode or Nyquist plot of the data from the EG&G PARC M388 Software system V2/70.

Stainless steel stirrers agitated the cell compartments on either side of the membrane which was secured between two halves of a

perspex cell. Cell volume was approximately 800 cm³ while the exposed membrane area disc was 51.6 cm². It was convenient to use Celgard 4510 as the hydrophobic membrane and Celgard 5511 for the studies on the hydrophilic membrane. All measurements were done at room temperature which was approximately 23°C.

Results and discussion

Hydrophobic membranes - Celgard 4510

In KCl solution, an examination of Bode plots revealed two time constants. These were at low frequency, less than 10 Hz and also at frequencies greater that 3 000 Hz. A high frequency relaxation of the double layer is expected but has not been fully investigated here. In the very dilute solutions studied, only a small contribution to the impedance spectrum from the double layer and cell geometry contribution would be expected from calculation.

Although there are three distinct regions in the Nyquist plot (2) due to different scales being required to emphasise this, only the largest feature is shown in Fig. 1, presented as a computer fit on the data. The minor features are not shown here. As the purpose of this paper is to characterise membranes into two distinct types a study of the minor features not due to the membrane was not done. A time dependence was exhibited in all experiments but after 4 h the rate of change was not marked.
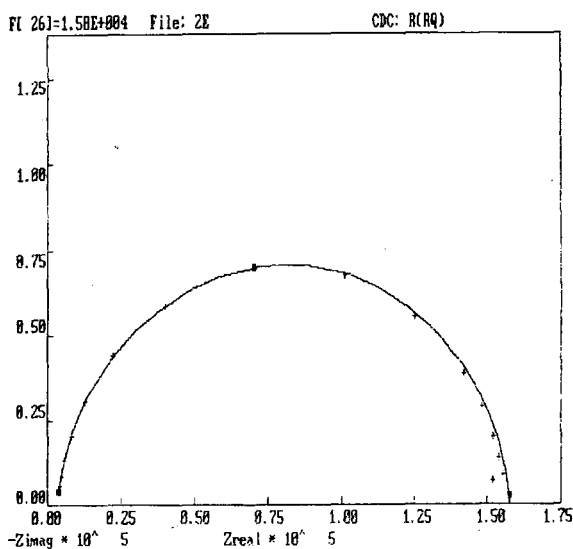
The effect of time dependence is discussed in detail in a subsequent section. In Fig. 1, which was computed using a commercial curve-fitting program from Boukamp (1989) the following data in Table 1 were obtained from 15 mg/l KCl electrolyte.

The equivalent circuit used is shown in Fig. 2. R_{elec} is the resistance due to cell geometry and due to the electrolyte compositions, R_p is the polarisation resistance at the aqueous/membrane interface; C_T is the double-layer capacitance. From the data in Table 1, the hydrophobic nature of the membrane is seen in the high resistance R_p which is also a function of electrolyte concentration but is emphasised at these low electrolyte concentrations.
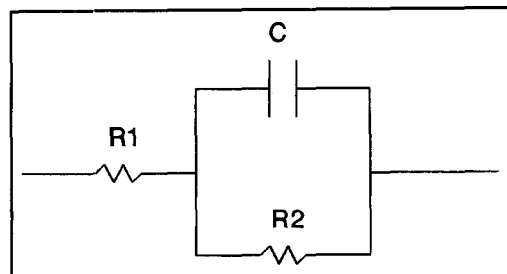

Figure 2
Simple model of the KCl/membrane interface

Hydrophilic membrane Celgard 5511

A typical Nyquist plot of the impedance in the complex plane for the Celgard 5511 membrane in a solution of 15 mg/l KCl is shown in Fig. 3.
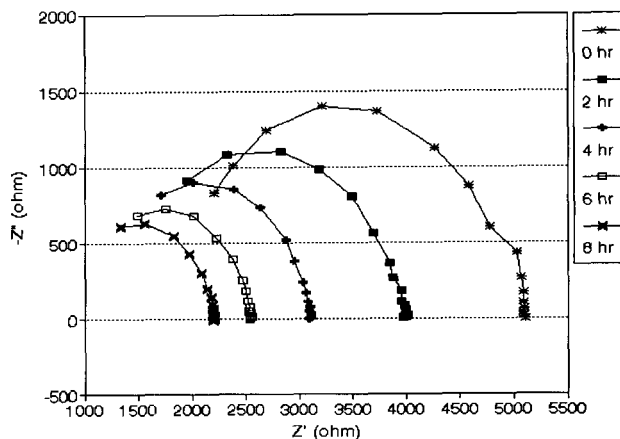

Figure 1
Computer fit for impedance data obtained with Celgard 4510 in 15 mg/l KCl.
(Dedicated system computer plot - unable to reproduce)

Figure 3
Time dependence of Celgard 5511 (hydrophilic) at 23°C in 15 mg/l KCl

TABLE 1 PARAMETERS OBTAINED FROM FIG. 1		
Parameter	**Parameter Value**	**Error**
R_{elec}	3 757 Ω	7.21
R_p	152 100 Ω	3.40
C_T	0.28 x 10⁻⁸ F/area	4.79

Several major differences may be seen when the hydrophilic and the hydrophobic systems are compared. While ionic concentrations in the double layer will be effectively the same as in the case of the hydrophobic membrane when the same concentrations of KCl are used, the membrane will be "seen" differently by means of the electrochemical impedance spectroscopy technique.

Impedance values of R_p are small compared with the hydrophobic membrane. Over the frequency range 10^{-3} Hz to 10^5 Hz, there is no high frequency behavior for the hydrophillic mem-

TABLE 2 COMPARISON OF HYDROPHOBIC AND HYDROPHILIC MEMBRANES				
Type of membrane	Concentration (mg/ℓ)	$R_1=R_{elec}$ (Ω)	$R_2=R_p$ (Ω)	C_T Farads/area
Hydrophilic Celgard 5110	1.5 10	1079 1660	3965 2005	0.58×10^{-9} 1.63×10^{-9}
Hydrophobic Celgard 4510	1.5 10	3918 3382	2.823×10^5 2.348×10^5	2.0×10^{-9} 3.54×10^{-9}

TABLE 3 COMPARISON OF MEMBRANES IN 15 mg/ℓ KCl SOLUTION				
	Amicon PM30	Millipore PTTK	Celgard 4510	Celgard 5511
$C_T(\mu F/m^2)$	1.98	0.9	0.68	0.32
Conductance (S/m^2)	0.53	1.52	3.25	1250

brane. An incomplete distorted semicircle suggests that the frequency range needs to be extended to above 10^5Hz. As there appears to be only one resistance-capacitance network partially resolved in Fig. 3 the intercept R_{elec} has to be estimated from a computer fit of the curve.

Based on values of R_p, alone, in dilute KCl solutions the ability to distinguish between hydrophobic and hydrophilic membranes using EIS is demonstrated. This method, once the membrane is available in the form of a sheet material, is fairly rapid.

Values of R_{elec} (corrected for time dependence) for the hydrophilic membrane, as might be expected, are close to those for the hydrophobic membrane. Thus the value of R_{elec} for the hydrophobic membrane at 3 162 Ω is close to the value of R_{elec} + R_p of 3 500 Ω for the hydrophilic membrane for the same concentration of 15 mg/ℓ KCl.

Table 2 shows typical values of capacitance C_T, $R_{elec} = R_1$, R_p = R_2 as a function of concentration as calculated by computer.

Data for ultrafiltration membranes in 15 mg/ℓKCl are available (Coster and Kim, 1992) and thus a comparison with Celgard membranes is possible.

The ultrafiltration membranes (Coster and Kim, 1992) Amicon PM30 and Millipore PTTK fall into the hydrophilic category. Hydrophobics capacitances are several times higher than those of the hydrophilic membrane 5511. Thus capacitance varies presumably according to the structure and surface difference associated with a particular membrane.

An important difference is that the capacitance of the double layer for the KCl/hydrophobic membrane is about twice that of the hydrophilic membrane, while R_{elec} values are not significantly different at high KCl concentrations. The R_p value is definitive in identifying the membrane type as can be seen from Table 1.

A change in ionic concentration from 1.5 mg/ℓ to 10 mg/ℓ results in significant changes in the capacity of the double layer. Studies are in progress to fit these capacities to a detailed model of the KCl/membrane interface.

Conclusions

Electrochemical impedance spectroscopy is a non-invasive technique which enables the rapid characterisation of membrane materials into the categories of hydrophobic or hydrophilic, without a microscopic analysis or other tests being required. On the basis of the parameters derived from the impedances, a model of the electrical double layer shows a difference in the capacitance which arises from the different surface structures of the membrane type.

Acknowledgments

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