

# 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 ultrafiltration 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 10 mV 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

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