



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# In situ characterization of compaction, ionic barrier and hydrodynamics of polyamide reverse osmosis membranes using electrical impedance spectroscopy

Terry C. Chilcott<sup>a,b,\*</sup>, Jie Cen<sup>a,c</sup>, John M. Kavanagh<sup>a</sup><sup>a</sup> School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia<sup>b</sup> UNESCO Centre for Membrane Science and Technology, The University of New South Wales, NSW 2052, Australia<sup>c</sup> Zhejiang University of Technology, 18 Chaowang Rd, Xiacheng, Hangzhou 310014, Zhejiang, China

## ARTICLE INFO

## Article history:

Received 23 August 2014

Received in revised form

11 December 2014

Accepted 13 December 2014

Available online 23 December 2014

## Keywords:

Reverse osmosis

Polyamide

Bipolar

Compaction

Electrical impedance spectroscopy

## ABSTRACT

The Maxwell–Wagner model facilitates discernment of differing electrical contributions of substructural layers in a membrane system from impedance spectra acquired from the whole system but in the absence of water fluxes. The fluxes manifest phenomenological contributions in the impedance spectra that can mask the substructural contributions. A model is presented that distinguishes between these contributions in spectra acquired from a thin-film-composite reverse osmosis polyamide membrane mounted in a cross-flow chamber that facilitated 4-terminal impedance measurements whilst sustaining pressures and steady state fluxes encountered in desalination plants. The phenomenological contributions were modelled with a simple electrical circuit comprised of inductive, conductive and generative components. The component values were strongly correlated with measurements of the water flux, which halved as the membrane was compacted at constant pressure. The unmasked Maxwell–Wagner contributions reflected realistic dielectric, conductive and geometrical properties of the filtration channel, membrane bulk and ionic barrier that were consistent with independent microscopic and spectroscopy characterizations. Changes in these properties and concomitant measurements of the membrane potential as the membrane performance approached the manufacturer's specification were consistent with an ion exclusion mechanism associated with a nanometer thick ionic depletion layer that manifests at the junction of the carboxyl-rich and amine-dominated regions of the polyamide active layer as the membrane compresses and hydrates.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The pre-treatment of reverse osmosis membranes in desalination modules with alcohol and water at atmospheric pressures aims to expel air trapped in the pores and interstitial spaces of the membranes that would otherwise block water fluxes. Further treatment at substantially higher pressures establishes more substantial fluxes to complete the expulsion and compress and hydrate the membrane into a state that maximizes salt rejection and water recovery. The latter treatment is often conducted over days to render the module operational. However, the electrochemical and physicochemical processes occurring during this phase have been neither characterized nor elucidated. This is principally because most methods of characterizing membranes involve comparisons of results acquired from

extracted membrane samples obtained before and after compaction phases. In contrast, electrical impedance spectroscopic (EIS) is a method that can be deployed in situ without disrupting desalination.

EIS has provided non-invasive means of probing membrane systems for almost a century. Some of the earliest studies were on suspensions of red blood cells, which yielded the first accurate estimates of the thickness of biologically functioning membranes [1] and an understanding of the biophysical relationships between membrane structure and function. Studies over the following decades characterized electrochemical interactions of ions, pharmaceuticals, toxins, etc. with, for example; cell membranes [2], cellular structures in living tissue [3] and the membranous surfaces of colloids in suspension [4]. Studies then progressed to other types of bio-membranes including plasmalemma and tonoplast membranes of single cells [5] and bilayer membranes reconstituted from lipids extracted from cellular membranes [6]. These characterizations provided bases to the development of electrochemical [7] and physicochemical [8] models explaining structural and functional rolls of membranes in cellular biology.

\* Corresponding author. Tel.: +61 408463761; fax: +61 293512854.

E-mail address: [terry.chilcott@sydney.edu.au](mailto:terry.chilcott@sydney.edu.au) (T.C. Chilcott).

Some of the rolls performed by biological membranes have application in industry. Examples of EIS studies performed on manufactured membranes include, for example, bipolar [9], ion-exchange [10,11], ultrafiltration [12], nanofiltration [13], and reverse osmosis [14]. However, the overwhelming characterization studies on these types of membranes utilize microscopy and other spectroscopy technologies that were developed many decades after EIS. A comprehensive and critical review of these technologies is given elsewhere [15].

### 1.1. State-of-the-art of structure of active layers of polyamide reverse osmosis membranes

The most recent microscopy and spectroscopy studies of particular relevance to the polyamide membrane used in this EIS study are a transmission electron microscopy (TEM) characterization [16] which has revealed an active layer comprised of a carboxyl-rich outer-region on top of an inter-region possessing amine-groups with a “sharp boundary” between these regions; modelling of the interfacial polymerization process during the manufacture of the membrane predicting these structural features [17]; and an X-Ray photoelectron spectroscopy (XPS) characterization [18] reporting the highest proportion of free carboxyl groups in the polyamide active layer.

The significance of juxtaposed carboxyl and amine regions to membrane functionality was first revealed in electrochemical [19] and impedance [20–23] modelling of electrophysiological [7,24,25] and EIS [26–28] characterizations of the plasmalemma membrane of living cells. The carboxyl and amine regions in biological membranes originate in the amino acids that comprise the polymer structure of membrane proteins. Such a protein is the proton-translocating ATP-synthase which catalyzes the biosynthesis of adenosine-triphosphate (ATP) from adenosine-di-phosphate ADP and phosphate, in which the juxtaposed carboxyl and amine regions feature in the membrane-spanning region of the ATP-synthase [29]. The juxtaposed regions also feature in bipolar membranes manufactured through the fusion of polymer cation- and anion-exchange membranes [30]. The common structures also reflect common functionalities involving the transport of water, rejection of ions of charge of either sign and the dissociation of water into  $H^+$  and  $OH^-$  ions [31,32]. These functions are associated with a narrow region that develops at the “sharp boundary” between the regions as hydration leads to the ionization of the carboxyl and amine groups and the creation of juxtaposed regions of fixed charge that are opposite in sign [7].

The type of membrane used in this study also shares a common structure with the biological and synthetic constructs as well as common functionalities, notably the functions of water-transport and ion-rejection that reflects the utilization of this type of membrane in desalination applications. These functionalities presumably have a similar origin in the narrow ion-rejecting region that would be expected to develop at the “sharp boundary” between the juxtaposed regions of charge of opposite sign. Indeed a recent EIS study [33] has characterized an ionic-barrier of “effective” thickness of only a few nanometers in isolated and partially hydrated active layers of membranes of similar type to that used in this study.

Fig. 1(b) features a schematic of the physicochemical (bipolar) structure for the active layer [16,17] upon which is superimposed the purported electrochemically induced depletion layer [7] that the analysis of impedance spectra herein indicates is the ionic-barrier [33].

### 1.2. State-of-the-art of impedance modelling of membrane systems in the presence of water fluxes

In this EIS study the measurements were not performed on isolated sections of membrane in the absence of water fluxes but on the intact and fully functioning membranes sustaining fluxes encountered in practice. The membranes were mounted in the Inphaze chamber depicted schematically in Fig. 1(a), which replicates the feed

and filtration dimensions as well as the operational and hydrodynamic features of membranes in spiral-wound modules but in a flatbed configuration. The chamber further incorporates four electrodes for measuring the impedance of systems in situ and facilitates simultaneous measurements of the filtrate flux.

The utilization of four electrodes in the flatbed configuration facilitates Maxwell–Wagner modelling of conductive and capacitive properties of layers comprising the system as represented by the  $g$ 's and  $c$ 's, respectively, in the Maxwell–Wagner model shown in Fig. 1(c). However, EIS characterizations using the Inphaze chamber report the evolution of phenomenological “inductive” and “generative” impedances [34,35] in the presence of water fluxes of the type that have been reported in earlier studies [10,34–38] of membrane systems. The origins of the phenomenological impedances have been attributed to coupling of water fluxes to the ionic flow generated by the impedance measurement, e.g. see [36,39]. The algorithms used to fit the Maxwell–Wagner model to the spectra have returned additional pseudoelements in which some of the values for the  $g$ 's and  $c$ 's in Fig. 1(c) are negative, which renders such elements uninterpretable as layers but transformable into “inductive” and “generative” components [40].

Herein these pseudo-Maxwell–Wagner elements are transformed into an equivalent circuit of “inductive”, “generative” and “conductive” components that reflect the theoretical frequency dependences of the phenomenological impedances on the coupling of the ionic and water fluxes [39]. The appropriateness of the circuit was gauged by the degree to which the component values correlated with water fluxes and the degree to which the Maxwell–Wagner elemental values reflected realistic structural and electrochemical properties of layers comprising the system over the compaction phase.

## 2. Material and methods

Following is a brief description of the experimental procedures covered in detail by Cen [41].

### 2.1. Inphaze filtration and impedance characterization chamber

Impedance characterizations of an AK reverse osmosis membrane (GE Osmonics) were performed in a stainless steel filtration cross-flow, flatbed chamber (Inphaze Pty Ltd., Sydney, Australia) shown schematically in Fig. 1(a). Two parallel electrode plates inject an *ac* electric current of uniform density through the membrane via the feed and filtrate solutions. Two separate and electrically isolated voltage-sensing electrodes located at the centers of the current-injecting electrodes monitor the response of the system to the injected current. The four-electrode configuration minimizes nuisance contributions to impedance measurements from the large and strongly frequency-dependent impedances of ionic double layers that form at the interfaces between the current injecting electrodes and the feed and filtrate solutions.

### 2.2. Solution and filtration operating conditions

The membrane was initially soaked in ethanol of purity greater than 90% for an hour, rinsed thoroughly in deionized water, stored in deionized water for 24 h and then mounted in the characterization chamber.

A sodium chloride feed solution of conductivity  $0.03 \text{ S m}^{-1}$  was stored in a 25 L enclosed tank. Water from a Julabo FL1201 cooler was recirculated through a heat exchange in the feed, which maintained the temperature at  $25 \pm 1 \text{ }^\circ\text{C}$ . A variable speed drive regulated pump (CAT Pump, model 277) operating at a pressure of 2000 kPa in conjunction with an air cylinder established a feed

# Forbidden

You don't have permission to access this resource.

---

*Apache/2.4.25 (Debian) Server at daneshyari.com Port 443*