In situ characterization of fouling in reverse osmosis membranes using electrical impedance spectroscopy

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Abstract. Analytical solutions of the Nernst-Plank, Poisson and continuity equations for a membrane undergoing reverse osmosis in a cross-flow system reveal that the flow of alternating ionic charge induced in the membrane during impedance measurements is actively assisted by the flow of water. The actively driven current manifested “inductive” responses in impedance measurements of a Filmtec BW30 reverse osmosis membrane mounted in an Inphaze flat-bed cross-flow module after 16 hours of filtering a mineral salt solution seeded with CaCl\textsubscript{2} and NaHCO\textsubscript{3} at pressure of 900 kPa. Fitted transfer functions resolved conduction and capacitive properties of four membrane layers, diffusion/concentration phenomenon and a pseudo “inductor” shunted by a conductor. A 10-fold decrease in the shunt conductance correlated with smaller increases in the conductance values for the filtrate and membranous layers, and the onset of fouling diagnosed by a rapid increase in flux decline.

1. Introduction

Membranes separate solutions of differing solute concentrations and thus are subject to differences in osmotic pressures arising from the membrane regulating solute and solvent flows that would otherwise allow the solutions to equilibrate. Extracellular “skeletons” in cellular systems and polymer composites in synthetic industrial systems elastically absorb osmotic as well as environmental and applied pressures that would otherwise rupture the membrane. So supported, membranes can sustain substantial pressure differences capable of reversing the direction of osmotically driven solvent flows whilst inhibiting solute flows. Such occurs in reverse osmosis membranes used in industry for desalination of seawater and recovery of water from industrial waste. Forward osmosis is an important function of ultrafiltration membranes used in hemodialysis treatments of the blood of patients suffering loss of kidney function.

A general deficiency of membrane systems is the accumulation of material and in some cases the eventual precipitation of soluble materials such as CaSO\textsubscript{4} or CaCO\textsubscript{3}, on the membrane surface. If not detected and removed in time, this can cause irreversible fouling of the membrane.

Presented here is an in situ electrical impedance characterization of a reverse osmosis system that is consistent with a theoretical analysis demonstrating the detectability of membrane fouling.
Figure 1

(b) Membrane layers & inductive impedance characterized by the modeling of the measurements in (a)

(c) Theory illustrating the origin of inductive phenomena

(d) Inductive shunt exhibits unique dependence on time, flux decline & fouling

(e) Dependence of inductance on time, flux decline & fouling

(a) Impedance measurements and Maxwell-Wagner & inductive modeling of RO membrane during fouling

Filtrate
Polyamide (PA) Active layer
PS microporous substrate
Polyester (PE) fabric support
Hydrophilic PVA film
Diffusion impedance
Inductive impedance

Water velocity $V$ ($10^{-4} \rightarrow 10^{-3}$ m/s)

Capacitive
Inductive

Constant $g$ (S/m²)

Time (Hours)

15 16 17 18 19 20 21

0 2 5 10

Impedance of the system (Ωm²)

Frequency (Hz)

10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6}

10^{2} 10^{3} 10^{4} 10^{5} 10^{6}

1.2 1.0 0.8 0.6 0.4

20 hours ($V=5\times10^{-4}$ m/s)

16 hours ($V=6.5\times10^{-4}$ m/s)

V=5\times10^{-4} m/s

V=6.5\times10^{-4} m/s

V=5\times10^{-4} m/s
2. Theory

Analytical solutions of the Nernst-Planck, Poisson and continuity equations [1] for a planar membrane of thickness $\lambda$, conductivity $\sigma$ and dielectric permittivity $\varepsilon$, mounted in a cross-flow system separating a feed solution of conductivity $\sigma_{\text{feed}}$ and a filtrate solution of surface conductivity $\sigma_{\text{filtrate}}$ yield the following expressions for the area specific impedance of the membrane in SI units of $\Omega \text{m}^2$, i.e.;

$$z_{\text{membrane}} = \frac{\lambda}{\sigma + j\omega \varepsilon} + z_v$$

where $\omega$ is the angular frequency in units of $\text{s}^{-1}$ and

$$z_v \equiv \frac{x_m \left( \frac{\lambda}{\lambda m} \right) - x_p \left( \frac{\lambda}{\lambda p} \right)}{\left( \frac{\sigma_{\text{feed}} + j\omega \varepsilon_{\text{water}}}{\sigma_{\text{filtrate}} + j\omega \varepsilon_{\text{water}}} \right)}$$

in which the Debye and characteristic lengths are defined in units of meters so;

$$\lambda_D \equiv \frac{ek^2}{2q^2\varepsilon}; \quad x_m \equiv \frac{2\lambda_D\sigma}{\sqrt{\nu^2\varepsilon^2 + 2\lambda_D^2\sigma(\sigma + j\omega \varepsilon) + \nu \varepsilon}}; \quad x_p \equiv \frac{2\lambda_D\sigma}{\sqrt{\nu^2\varepsilon^2 + 2\lambda_D^2\sigma(\sigma + j\omega \varepsilon) + \nu \varepsilon}}$$

$V$ is the velocity of water in units of $\text{ms}^{-1}$ (as distinct from the cross-flow velocity), $C$ the ionic concentration in the membrane ($\text{m}^{-3}$), $k$ the Boltzmann constant (1.38x$10^{-23}$ J/K), $T$ the temperature (300 K) and $q$ the magnitude of the electronic charge (1.602x$10^{-19}$ C). The first term in Equation (1) derives exclusively from conductive, dielectric and geometrical properties of the membrane as described by a Maxwell-Wagner layer of conductance and capacitance per area given by, respectively;

$$g = \frac{\sigma}{\lambda_D} \quad \text{and} \quad c = \frac{\varepsilon}{\lambda_D}$$

The second term, $z_v$, derives from the flow of alternating ionic charge induced in the membrane during impedance measurements that will be actively driven by the flow of water. Equations (2) and (3) reveal the dependency of this term on the velocity $V$ of the water and in particular on $\sigma_{\text{feed}}$ and $\sigma_{\text{filtrate}}$ at the respective membrane surfaces. $\sigma_{\text{feed}}$ is characteristically greater than $\sigma_{\text{filtrate}}$ and $\sigma$, which effectively eliminates the contribution of the feed as a Maxwell-Wagner layer from the impedance measurements. Thus the impedance of this simplified membrane system is essentially given by;

$$z_{\text{system}} \approx \frac{\lambda}{\sigma + j\omega \varepsilon} + z_v \left( \frac{\sigma_{\text{feed}}}{\sigma_{\text{filtrate}} + j\omega \varepsilon_{\text{water}}} \right)$$

where the dependency of $z_v$ on $\sigma_{\text{feed}}$ at the membrane surface, where ions will concentrate and promote precipitation, potentially provides a means of monitoring the degree of fouling in the system.

3. Materials and Methods

Filtration experiments were performed in an Inphaze stainless steel flat-bed cross-flow filtration module that facilitates simultaneous measurements of impedance and water velocity as described in detail by Antony et al [2]. The feed and filtration channels in the module are 310 mm long, 60 mm wide and 0.80 mm thick and separated by a supported membrane of operational area of 0.0124 m$^2$. The opposing faces of the channels contain stainless steel electrodes of comparable area to the membrane, which were used to inject a range of electrical current stimuli of differing frequency but uniform density through the feed, membrane and filtrate system. Insulated small voids located centrally in these electrodes, support voltage-sensing electrodes that monitored the voltage responses of the system to the stimuli, independently of the strongly frequency-dependent responses of the ionic double layers that form between the current-injecting electrodes and solutions. The amplitudes and phase differences of stimuli and responses were measured with an impedance spectrometer (Inphaze Pty Ltd Australia).

The Filmtec BW30 reverse osmosis membranes were preconditioned and compacted in deionised water (Millipore, Australia) for 24 hours until a stable permeate flux of deionized water was reached. Filtration, water flow and impedance measurements were performed simultaneously using a feed seeded with CaCl$_2$ and NaHCO$_3$ at, cross-flow velocity of 0.2 ms$^{-1}$, 20$^\circ$C and 900 kPa.
4. Results and Discussion

The magnitudes and phases of impedances of frequencies from 1 to $10^6$ Hz were acquired using an Inphaze spectrometer every 15 minutes after 15 hours of filtration. Transfer functions of the form;

\[
Z_{TF} = \frac{1}{g_1} + \sum_{k=2}^{5} \frac{1}{g_k+\omega c_k} + \frac{1}{g_6+\omega c_6} + \frac{1}{g_7+\omega c_7} + \frac{1}{g_8+\omega c_8}
\]  

(6)

were fitted to the mean and standard deviation values of every three consecutive spectra. Reduced-$\chi^2$ statistics [3] provided justification for the fits which are shown in Figure 1(a).

The transfer function is a general form of the Maxwell-Wagner model used to characterize spectra over the first 16 hours of filtration [2] (e.g. see 1st spectrum in Figure 1(a)). In common are the 1st term attributed principally to the filtrate, the next four terms ($k=2$…5) attributed to sub-structural layers of the membrane as assigned in Figure 1(b) and the 6th term attributed to concentration/diffusion polarization effects that exhibit a similar dependency on frequency to that of a Maxwell-Wagner layer [4]. The 7th term exhibits a different frequency dependency to that of a Maxwell-Wagner layer, which becomes discernable in spectra acquired after 16 hours in Figure 1(a) as positive slopes in the impedance dispersions with frequency in the range of $10^5$-$10^6$ Hz. This type of dispersion has been reported in other membrane systems [2,5,6,7,8] and described as pseudo “inductive” phenomenon.

Figure 1(c) reveals similar “inductive” phenomena in theoretical dispersions of Equation (5) for a membrane of comparable bulk electrical properties covering ranges of frequency and water flux encountered experimentally and a value for $\sigma_{fod}$ reflecting fouling conditions at the membrane surface diagnosed by a by a rapid increase in flux decline. The generally consistency of theory with experiments suggests that the “inductive” behavior is attributable to the term $z_V$ in Equation (5), which Equation (2) reveals exhibits different dependencies on frequency to that of a Maxwell-Wagner layer.

Whilst the capacitance values in Equation (6) did not vary significantly from the values shown in Figure 1(b), the time-courses of the conductance values shown in Figure 1(d) reveal that conductance values for the filtrate, membranous layers as well as the diffusion/polarization impedance generally increased with time as the flux declined. However, the most sensitive variation with increasing flux decline was the 10-fold decrease in values for $g_7$, the conductor shunting the inductor $l_7$.

5. Conclusions

Pseudo “inductive” phenomena in impedance measurements of membrane systems can arise from alternating ionic charge induced by these measurements that is actively driven by flows of water established by applied and osmotic pressures. Characterizations of the phenomena can quantify properties of the system that are potentially predicative of membrane fouling. Further detailed theoretical analyses of the origins of the phenomena can improve predictability.

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