Exploration of high resolution electrical impedance spectroscopy technique for study of membrane wetting for Forward Osmosis

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Introduction

Forward osmosis (FO) is viewed as a promising membrane technology for water supply, and utilises osmotic driving force for separation. The attractiveness of FO is that no application of hydraulic pressure is necessary, and this would result in lower electrical energy demand compared to conventional water technologies (Cath et al., 2006). However, progress in this technology has pointed out areas that need development. A recent study discussed that one area is to improve wetting of the FO membranes in order to enhance osmotic transport (McCutcheon and Elimelech, 2008). Inadequately wetted membranes would mean that vapour and/or air trapped within the membrane structure would obstruct water transport and aggravate internal concentration polarisation within the support layer. The effect is diminished driving force and lower water production. However, while the immediate benefit of increasing water flux with membrane wetting is obvious, another side effect that may result from this form of membrane conditioning for FO, such as increased salt transmission from the draw solution into the feed solution, has not been adequately addressed. As FO membranes are dense and have "pores" in the nanometer range, it would be advantageous to apply a high resolution technique to gain deeper insight into the phenomenon. For this purpose, the electrical impedance spectroscopy (EIS) has been recognised as a feasible non-invasive and sensitive analytical technique for membrane processes, and can potentially detect substructure features of the order of a Debye length (~ 1 nm) (Coster et al., 1996; Chilcott et al., 2002; Gaedt et al., 2002). This study explores the use of high resolution EIS technique for investigation of membrane wetting for FO processes.

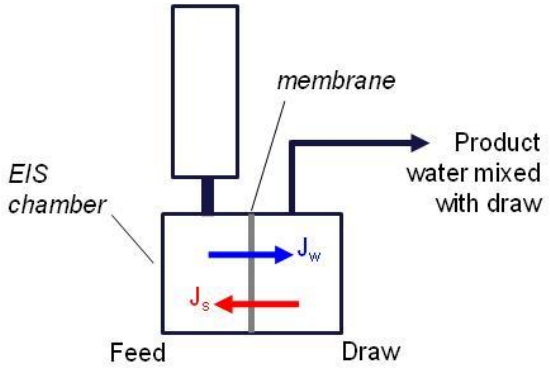
Materials and methods

The EIS experiments were conducted using the spectrometer system supplied by INPHAZE Pty Ltd, and is depicted in Figure 1. The EIS equipment measures conductance and capacitance across the membrane sample over varying frequencies, and derives the system impedance based on the Maxwell-Wagner model as follows:

$$Z = \sum_{k=1}^{K} Z_k = \sum_{k=1}^{K} \frac{1}{G_k + j\omega C_k} \qquad (1)$$

In this study the feed solution was 1 gL^{-1} of NaCl solution, and the draw solution was 0.5 molal NaCl that provided a bulk osmotic driving force of about 22 bar. A reservoir was attached to the feed side to provide adequate supply of feed water for permeation through the membrane.

Product water was collected on the draw side, and weighed regularly using an electronic balance. Water flux (J_w) was derived from the mass obtained in the time interval between 15 and 30 minutes after begin of each experiment. This was to allow for flux stabilisation, and to avoid possible experimental errors associated with system start-up, while dilution and concentration effects of the draw and feed solutions were still relatively moderate. Salt flux (J_s) was derived based on conductivity measurement of the feed solution at the begin and end of each experiment.



Experiment type	*Batch*
Initial feed volume	*43 mL*
Initial draw volume	*13 mL*
Initial feed concentration	*1 gL^{-1} NaCl*
Initial draw concentration	*0.5 m NaCl*
Membrane area	*5.37 cm^2*
Membrane orientation	*Skin against feed*

Figure 1: Experimental set-up and parameters

A standard protocol for membrane wetting was consistently applied: freshly cut FO membrane (cartridge type, provided by Hydration Technologies Innovations) was first rinsed with Milli-Q water (MQ), and then soaked for 1 hour in the wetting agent , before it was stored in MQ at 4℃ prior to the experiments. In this study, ethanol solutions (EtOH) of concentration ranging from 0 % (MQ only) to 100 % (EtOH only) were used as the wetting agent. In general, each EIS experiment run comprised three spectra in the frequency range from $1.86 \cdot 10^{-2}$ to $9.84 \cdot 10^{5}$ Hz, and each run was furthermore repeated to ensure consistency and reproducibility. For the purpose of presentation, however, only one experiment run for each condition was shown.

All chemicals used in this study were of analytical grade. The programme OLI Analyzer 3.1 (OLI Systems Inc.) was used for the calculation of osmotic pressures. Scanning Electron Microscopy (SEM) examination was conducted using a Zeiss EVO 50.

Concomitantly, to investigate the effects of wetting on the rejection layer (“skin”) versus that on the support layer (“support”) of the FO membrane, reverse osmosis (RO) experiments were conducted for the conditions of MQ (0% EtOH) and 40% EtOH. Description of the RO system can be found in our previous publication (Lay et al., 2010). The objective of the RO experiments was to determine water permeability coefficient (A) and salt permeability coefficient (B) of the membrane skin subject to different wetting treatment. The solution-diffusion model gives the following relationships.

$$A = \frac{J_w}{\Delta p} \qquad (2)$$

$$B = \frac{(1-R)}{R} \cdot A \cdot (\Delta p - \Delta \pi) \qquad (3)$$

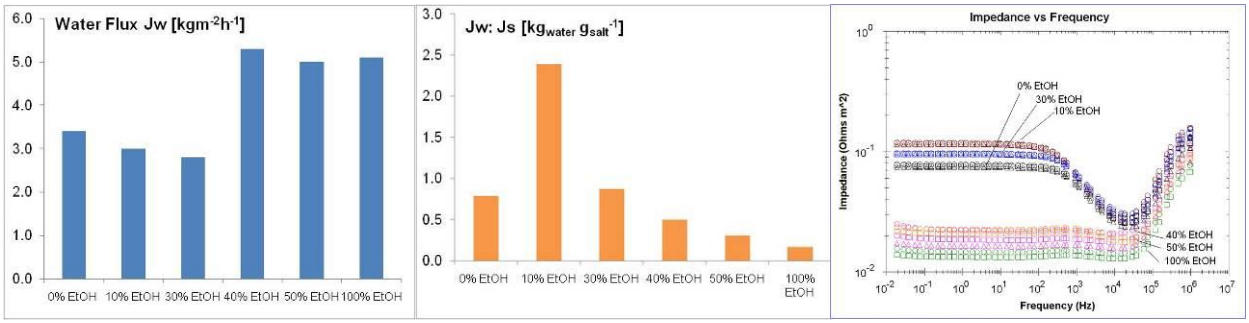
Results and discussion

EIS Analysis

The EIS experiments showed wetting with EtOH has distinctive effects on the FO membranes. From Figure 2 (a), it appears that there could have been a critical wetting condition between 30% and 40% EtOH concentration. Below this concentration, increasing EtOH concentration reduced J_w, whereas above this concentration, increasing EtOH concentration increased J_w. However, further analysis provided interesting insight. The ratio J_w:J_s – Figure 2 (b) – has practical significance for FO, and can be related to intrinsic membrane properties by applying the van't Hoff relation as given in equation (4 **)**. Ideally, a FO process should have a J_w:J_s ratio (~ A/B) that is as high as possible (Lee et al., 1981; Cath et al., 2006).

$$\frac{J_w}{J_s} = \frac{R_{id} \cdot T \cdot A}{B} \qquad (4)$$

The EIS analysis corroborated the above findings. As observed in Figure 2 (c), while the EIS spectra showed a distinct step change in the impedance below 10^3 Hz between 30% and 40% EtOH corresponding to the profile of J_w, the order of the spectra – interestingly – did not correspond to that of J_w, but rather to that of J_w:J_s. Such observation may be attributable to membrane swelling under the action of EtOH. At low concentrations, EtOH could have a homogenising effect on the membrane structure, which was of cellulose triacetate material (Cai et al., 2002). At high concentrations, however, EtOH could have a damaging effect and could cause alteration of the pore structure (Tsui and Cheryan, 2004).

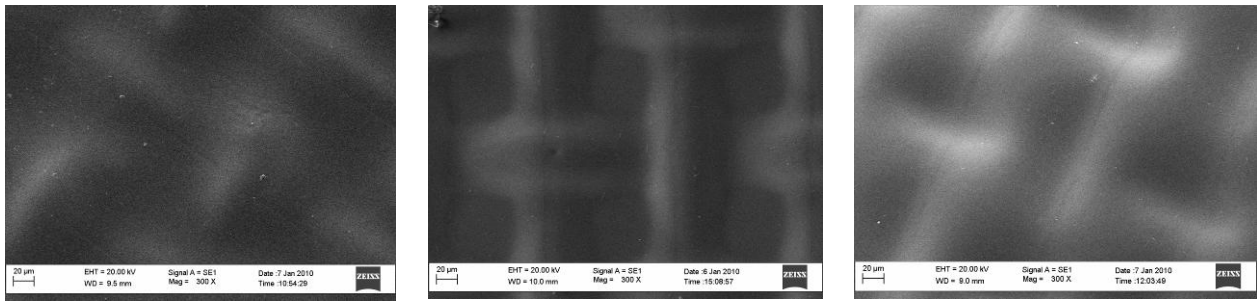


(a) (b) (c)

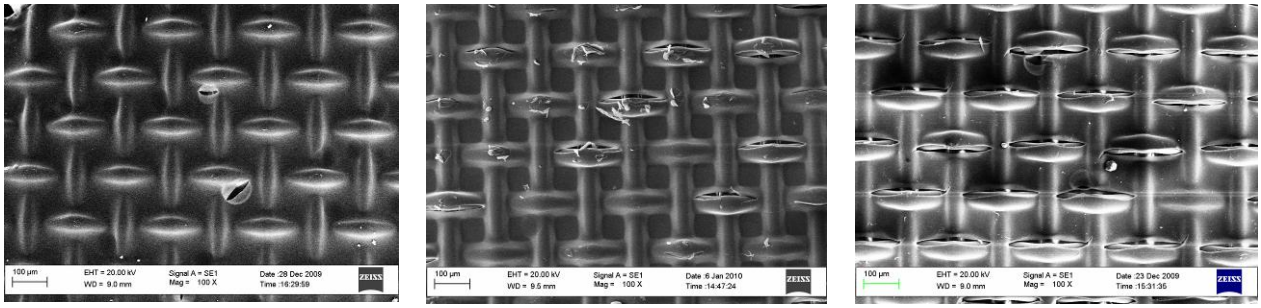
Figure 2: EIS experiments: (a) Water fluxes (b) J_w:J_s ratio and (c) EIS spectra for FO membranes wetted with different EtOH concentrations

SEM Examination

From Figure 3, the SEM images did not reveal noticeable differences in the membrane "skin" for the different EtOH concentrations. However, SEM images of the "support" side showed visible changes in the pore structure with increasing EtOH concentration.



(a-i) 0% EtOH – "Skin" (b-i) 40% EtOH – "Skin" (c-i) 100% EtOH – "Skin"

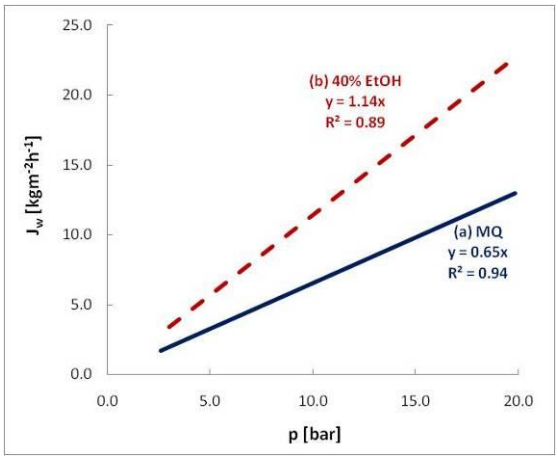


(a-ii) 0% EtOH – "Support" (b-ii) 40% EtOH – "Support" (c-ii) 100% EtOH – "Support"

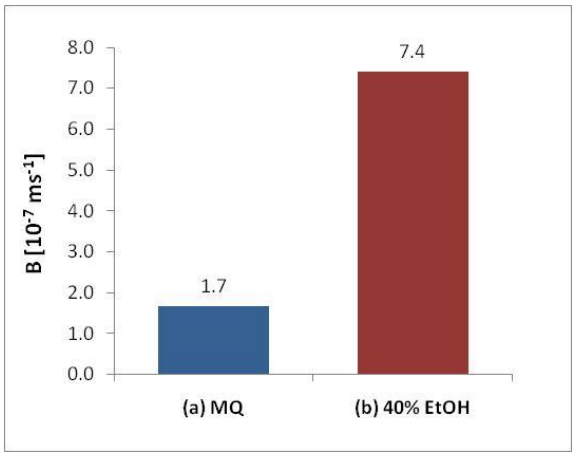
Figure 3: SEM images of membranes wetted with different EtOH concentrations (a)-(c), and as viewed from (i) "skin" and (ii) "support"

RO Experiments

The RO experiments confirmed the effects of EtOH on the membrane "skin". While water permeation was greater for wetting with 40% EtOH as compared to MQ (Figure 4 (a)), the corresponding effect on salt transmission was disproportionately greater and increased more than four-fold (Figure 4 (b)).



Water permeability coefficient (A)



Salt permeability coefficient (B)

Figure 4: Derived membrane coefficients from RO experiments for membranes wetted with (a) MQ and (b) 40% EtOH

Conclusions

The EIS technique has demonstrated that it can sensitively detect the effects of membrane wetting for forward osmosis, which corresponded to changes in the properties of both the "skin" and the "support" layer as verified independently by SEM examination and RO experiments. Ongoing work will investigate the effects of various wetting agents with regards to enhancing membrane properties for optimal FO performance.

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Symbols

A	Water permeability coefficient	R	Salt rejection
B	Salt permeability coefficient	R_{id}	Ideal gas constant
C_k	conductance of an element k	t	Time
G_k	capacitance of an element k	T	Temperature
J_s	Salt flux	Z	Impedance
J_w	Water flux	ω	angular frequency of alternating current
p	Hydraulic pressure	π	Osmotic pressure

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