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Reliable, Bench-Top Measurements of Charge Density in the Active Layers of Thin-Film Composite and Nanocomposite Membranes Using Quartz Crystal Microbalance Technology

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Abstract: A reliable, user-friendly, bench-top method was developed and evaluated for the measurement of negative charge density in the active layers of thin-film composite and thin-film nanocomposite membranes. The method consists of isolating the active layer on a quartz crystal microbalance (QCM) sensor (*i.e.*, AL+sensor sample), exposing the AL+sensor sample to an aqueous cesium solution at any pH of interest, and measuring with a QCM the mass of cesium ion that associates with the negative sites of the active layer. Results showed that QCM measurements of charge density in active layers were: (1) repeatable within 3% for tests performed with the same AL+sensor sample under the same experimental conditions; (2) reproducible within 3.8% for tests performed with the same AL+sensor sample when the ionic strength of cesium solutions was varied by 300%; (3) reproducible within 4% for active layers isolated from nearby locations of

the same membrane sheet; and (4) consistent within 2.1% at pH = 10.5 with results obtained using the previously reported Rutherford backscattering spectrometry method on non-isolated active layers. The results therefore demonstrate the robustness, repeatability, reproducibility, and accuracy of the QCM method. We also demonstrated that the ionization behaviors of the polyamide-based thin-film composite and nanocomposite membranes tested were similar: both membranes had bimodal pK_a distributions and negative charge densities of ≈ 0.5 M at full ionization.

Keywords: thin-film composite; nanocomposite; membrane; quartz crystal microbalance; charge density

1. Introduction

Thin-film composite (TFC) membranes are commonly used in reverse osmosis (RO), nanofiltration (NF), forward osmosis (FO), and other membrane-based separation processes [1-4] for a broad range of applications such as water desalination and reuse [1, 3, 5], treatment of industrial wastewater [6, 7], liquid food processing [8-10], and energy production [11-13]. TFC membranes commonly consist of a top ultrathin (≈ 20 -200 nm) active layer made of polyamide, supported by a porous polysulfone support (≈ 30 μm) backed by non-woven polyester fibers (≈ 200 μm) [1, 14]. A

recent variation of TFC membranes, with the potential to deliver higher water permeability with minimal changes in salt rejection, are thin-film nanocomposite (TFN) membranes which have nanoparticles (*e.g.*, titanium dioxide, zeolites, carbon nanotubes) embedded within the active layer polymer matrix [14-18]. In both TFC and TFN membranes, the active layer is the main barrier to the permeation of water and solutes [1, 15], and charge density is one of the active layer properties that determines membrane performance [1, 14, 19-21].

Charge density in the polyamide matrix of TFC and TFN active layers is the result of the ionization of carboxylic and amine groups that are the product of the incomplete crosslinking of reactants during active layer casting [1, 14]. In TFN membranes, charged sites may also be contributed by the nanoparticles [16, 22]. Since a larger charge density is the result of a lower degree of polyamide crosslinking [1, 14, 23], charge density is related to pore structure and size exclusion of contaminants [1, 20, 24]. Charge density also affects membrane surface hydrophilicity [1, 25], electrostatic interactions with foulants [21, 26, 27], and electrostatic exclusion of ionic contaminants [14, 19, 20]. Charged sites are also sometimes used as reactive sites for membrane modification [28-30]. As a result, reliable, user-friendly

methods for the quantification of charge density in active layers can serve as useful tools to accelerate the development of TFC and TFN membranes.

Different procedures have been used to measure charge density in the active layers of TFC membranes [23, 25, 31-33]. The reported procedures can be classified into those that measure the volume-averaged charge density of the active layer [23, 31, 33] and those that measure the surface charge density [25, 32, 33]. In this study, we focus on the quantification of the volume-averaged charge density of the active layer, for which the main technical obstacle is that the active layer must be resolved from the rest of the membrane. This obstacle has been overcome by two methods [23, 33], both of which tagged ionized functional groups in the active layer using ions and subsequently quantified the concentration of tagging ions in the active layer.

The first method [23, 24] characterized the ionization behavior of various commercial TFC membranes as a function of pH by using silver (Ag^+) and tungstate (WO_4^{2-}) ions to tag negatively ionized carboxylic groups and positively ionized amine groups, respectively, through ionic association.

The concentration of silver and tungstate ions in the active layer was subsequently quantified using Rutherford backscattering spectrometry (RBS). Unfortunately, while the ion probing+RBS method is precise and

reliable, RBS analysis requires specialized expensive instrumentation [33]. The second method [33] used uranyl (UO_2^{2+}) ion to tag carboxylic groups via complexation, and subsequently quantified the concentration of uranyl ions in the active layer using liquid scintillation counting. One important drawback of the uranyl method towards the study of membrane charge is that it measures only the total concentration of carboxylic groups [33] (*i.e.*, ionized plus non-ionized groups) and therefore only quantifies charge density at full ionization, which for most cases occurs at $\text{pH} > 10$ [23, 24].

One technology that has not been explored to measure charge density in active layers is quartz crystal microbalance (QCM) technology [34-36]. The sensitivity of current QCM equipment should be able to detect tagging ions and molecules such as those used in the ion probing+RBS and uranyl binding methods. For example, the areal mass of silver ions that would saturate the negative sites of a polyamide active layer with a thickness of 100 nm and carboxylic group concentration of 0.5 M, which are within the range of values reported in the literature [24], would be 540 ng/cm^2 ; this areal mass is well above the few ng/cm^2 detection limit of current QCM equipment [35]. Given that QCM operation requires that any mass added to a microbalance sensor be much lower than the mass of the sensor itself [34-36], the active layer would need to be isolated on the sensor without the

much heavier polysulfone and polyester support layers. Such an obstacle is not un-surmountable as evidence of successful isolation of polyamide active layers on silicon and zinc selenide (ZnSe) surfaces, and on polyimide-coated microbalance sensors, already exists in the literature [37-40].

Accordingly, the objective of this study was to develop a method to reliably measure the volume-averaged charge density in the active layers of TFC and TFN membranes as a function of pH by first isolating the active layer on microbalance sensors, and then using QCM equipment to measure the areal mass (ng/cm^2) of an ion probe that saturates the charged sites in the isolated active layers. Given that in the pH range of interest for water treatment ($\text{pH} > 6$), the concentration of positively charged sites ($< 0.004\text{M}$) in the active layers of TFC membranes is negligible compared to the concentration of negatively charged sites ($> 0.1\text{ M}$) [23, 24], this study focused on the quantification of negative charge density. Procedures for membrane sample preparation and testing, illustrative results, and evidence of reliability, repeatability, reproducibility, and accuracy are presented.

2. Materials and Methods

2.1. Chemicals and solvents

A.C.S. certified cesium chloride (CsCl , 99.999%), cesium hydroxide (CsOH , 99.95%) and silver nitrate (AgNO_3 , 99%+) were obtained from Sigma Aldrich (Saint Louis, MO). HPLC grade dimethylformamide (DMF), and A.C.S. certified nitric acid (HNO_3 , 70%), hydrochloric acid (HCl , 37%), ethanol (95%), hydrogen peroxide (30%) and ammonium hydroxide (25%) were acquired from Fisher Scientific (Pittsburgh, PA). All chemicals and solvents were used as received from the manufacturer without further purification.

2.2. Membranes

A thin-film composite (TFC) membrane and a thin-film nanocomposite (TFN) membrane were studied. Since most commercial TFC membranes have polyamide active layers, the TFC membrane tested was the ESPA3 RO membrane (Hydranautics, Oceanside, CA) which has a fully-aromatic polyamide active layer [24]. The active layer of the TFN membrane tested consisted of LTA zeolite nanoparticles embedded in a fully-aromatic polyamide matrix at a concentration of 0.76 %w/w. The TFN membrane was prepared as described elsewhere [18] and was received from the Lind Laboratory at Arizona State University (Tempe, AZ). Both membranes were stored at $4.4 \pm 0.5^\circ\text{C}$ upon receipt. The membrane samples whose

active layers were isolated on microbalance sensors or silicon wafers consisted of $2.5 \times 5.0 \text{ cm}^2$ coupons cut from a TFC spiral-wound element and a TFN flat sheet sample. Prior to use, the membrane coupons were thoroughly rinsed with ultrapure water ($\geq 17.8 \text{ M}\Omega \cdot \text{cm}$), and then stored also in ultrapure water in amber glass bottles.

2.3. Cleaning procedure for microbalance sensors and silicon wafers

Membrane active layers were isolated on quartz crystal microbalance (QCM) sensors or silicon wafers. The sensors (Biolin Scientific, Lithicum Heights, MD) were 14 mm in diameter and had a root-mean-square roughness of $\approx 3 \text{ nm}$, a gold coating (100 nm), an AT crystal cut, and a resonance frequency of $4.95 \text{ MHz} \pm 50 \text{ kHz}$. The silicon wafers had a polished surface onto which the active layers were isolated. The preparation of sensors and silicon wafers prior to active layer isolation was identical: (1) exposure for 10 minutes (with the gold surface facing up for sensors) to both ozone and ultraviolet light (185-254 nm) (PROCLEANER, Bioforce Nanosciences, Ames, IA); (2) immersion for 5 min in a 75°C 5:1:1 solution of ultrapure water, ammonium hydroxide (25%) and hydrogen peroxide (30%), respectively; (3) thorough rinse with ultrapure water; (4) drying with

ultrapure nitrogen; and (5) repeat of step 1. The sensors were the stored in sealed plastic boxes for no more than 24 hours before use.

2.4. Active layer isolation

Membrane coupons were thoroughly rinsed with fresh ultrapure water and then dried by placing the coupons between two pieces of Whatman filter paper No. 1 (GE Healthcare, Piscataway, NJ), and applying fingertip pressure. The procedure used to isolate the active layers of membrane coupons was based on the use of dimethylformamide (DMF) for dissolution of the polysulfone support as described elsewhere [37-39]. We describe the procedure used for the isolation of active layers on QCM sensors, and the same procedure was used to isolate active layers on silicon wafers.

Figure 1. Schematic of the procedure used for the isolation of active layers of thin-film composite (TFC) and thin-film nanocomposite (TFN) membranes on quartz crystal microbalance (QCM) sensors and silicon wafers. (a) The polyester backing is peeled off from the active layer and polysulfone support. (b) The membrane coupon minus polyester backing is placed against the QCM sensor with the active layer facing the sensor. (b-c) The membrane coupon and sensor are secured to each other using a custom stainless steel (SS) 316 assembly, and (c) the polysulfone support is dissolved using dimethylformamide (DMF). (d) The final product is the isolated active layer on the QCM sensor (AL+sensor sample).

At a corner of the membrane coupons, the polyester layer was separated from the rest of the membrane using a clean thin knife blade, and the polyester layer was then completely peeled off by hand. The active layer side of the membrane coupon without the polyester layer (Figure 1a) was placed against the gold surface of the QCM sensor resting on a custom $4.5 \times 4.5 \text{ cm}^2$ stainless steel 316 support (Figure 1b). Next, 3-5 drops of ethanol were added on the polysulfone side of the membrane to flatten the

membrane against the sensor surface. The membrane and sensor were then sandwiched between the square stainless steel support and a custom 4.5×4.5 cm^2 stainless steel 316 frame that had an inner 2×2 cm^2 opening that allowed access to the membrane and sensor (Figure 1c). The metal support and frame were secured to each other using six screws. The polysulfone support was then dissolved using the following sequence a total of 25 times: drop-wise addition of 2 ml of DMF, let stand for 1 minute, disposal of the DMF-polysulfone solution by tilting the stainless steel assembly, and absorption of the remaining DMF-polysulfone solution at one of the corners of the stainless steel frame using a KIMWIPES tissue. The custom stainless steel assembly allowed us to ensure consistency in the active layer isolation procedure among different membrane coupons.

After dissolution of the polysulfone layer, the assembly was allowed to dry in air overnight, and a scalpel was used to cut the active layer at the edge of the sensor where necessary to free the sensor from the metal base. After removing the top stainless steel frame, the active layer-coated sensor, referred to as the AL+sensor sample, was dipped in 50 ml of DMF and gently agitated for ≈ 5 min. This step was repeated with fresh DMF two additional times, after which the sensor was allowed to dry in air overnight. Next, the AL+sensor sample was immersed in 50 ml of fresh DMF

undisturbed for 4 hours, removed, allowed to dry in air, thoroughly rinsed with ultrapure water and dried with ultrapure nitrogen. The dried AL+sensor sample (Figure 1d) was stored in a sealed plastic box until further use.

2.5. QCM analyses

QCM analyses were performed in air and aqueous solution using a Q-Sense E4 quartz crystal microbalance (Biolin Scientific, Lithicum Heights, MD). The E4 microbalance has four modules that allowed for simultaneous testing with the same test solution of up to four sensors, one of which always corresponded to a control sensor (*i.e.*, without isolated active layer). Aqueous solutions were always degassed in a FISHERBRAND FS30 sonicator bath (Fisher Scientific) for approximately 30 minutes before use. All tests were performed in continuous flow mode (0.1 mL/min) at $22\pm0.02^{\circ}\text{C}$, and prior to all tests, the frequency of vibration of the sensors was monitored for 20 minutes in both air and ultrapure water to ensure stability of readings. During experiments, AL+sensor samples were exposed to various test solutions. For each test solution, data was continuously collected until the AL+sensor samples and test solution reached equilibrium as defined by a rate of change of areal mass lower than $0.25\text{ ng/cm}^2/\text{min}$.

This definition ensured that when the test solution was changed, the detected mass change during the previous 4-minute period was lower than the sensitivity of QCM measurements in ultrapure water for AL+sensor samples ($\approx 1.0 \text{ ng/cm}^2$). Additionally, this approach generally meant that exposure to any given test solution ended when no more than an additional 2% in mass change was expected in the subsequent 60 minutes. The conditions described above were usually met within 60 minutes of contact time with a test solution. Once the QCM reading was stable, the AL+sensor sample could be exposed to a new test solution.

One objective of QCM analyses was to measure the areal mass of active layers ($m_{\text{AL,areal}}$) of TFC and TFN membranes isolated on quartz crystal sensors. The $m_{\text{AL,areal}}$ values were obtained based on the difference between microbalance readings for the sensors in air before and after active layer isolation. For each sample, four measurements were taken each before and after active layer isolation to obtain the uncertainty in the mass of active layer isolated.

The main objective of QCM analyses was to measure the areal mass of cesium ion ($m_{\text{Cs,areal}}$) that ionically associated with negatively charged sites in TFC and TFN active layers. The $m_{\text{Cs,areal}}$ values were obtained based on the

difference between microbalance readings for AL+sensor samples in ultrapure water and in aqueous cesium solutions. When the objective of the test was to measure $m_{\text{Cs,areal}}$ at $\text{pH} \approx 10.50$, the test consisted of five cycles of exposure to aqueous CsOH solution and ultrapure water. Other tests had the objective of assessing $m_{\text{Cs,areal}}$ at various pH conditions in the pH range of 4.89-10.62, and were performed as follows: (1) three initial cycles of exposure to CsOH solution at $\text{pH} \approx 10.50$ and ultrapure water; (2) depression of the pH of the CsOH solution to the next pH of interest using concentrated hydrochloric acid (HCl); (3) one cycle of exposure to the CsOH solution at the newly adjusted pH followed by exposure to ultrapure water; and (4) iteration of steps 3 and 4 at the remaining pH conditions of interest. QCM tests were also performed to assess the effect of the concentration of cesium in solution on the measured $m_{\text{Cs,areal}}$ value; the cesium concentration was adjusted using CsCl concentrations in the 0.5-2.0 mM range and the experimental pH value of cesium solutions was in the range of 10.48-10.54.

2.6. Ion-probe solutions

Solutions containing cesium (Cs^+) or silver (Ag^+) ions as ion probes of interest were prepared by dissolving cesium chloride (CsCl), cesium hydroxide (CsOH) or silver nitrate (AgNO_3) in ultrapure water. The pH of

the cesium solutions was adjusted by addition of HCl or CsOH, and the pH of the silver solutions was adjusted by addition of nitric acid (HNO₃) or sodium hydroxide (NaOH). Silver solutions were prepared and used under dim red light environment to avoid photo-reactivity. The concentrations of cesium ($<6 \times 10^{-3}$ M) and silver ($<10^{-5}$ M) in solution were always below their solubility limits [41]. Cesium solutions were used in microbalance tests as described in Section 2.5, and silver solutions were used for ion probing+RBS analyses as described in Section 2.7.

There are two factors that could potentially prevent cesium or silver ions from accessing all charged sites throughout the active layers: steric effects and kinetic limitations. Steric effects are minimized by the smaller ionic radius of cesium (<1.7 Å [42]) and silver (<1.42 Å [43]) compared to the pore radii (>2.1 Å [44-46]) in polyamide active layers. Kinetic limitations were circumvented by providing total contact times (≈ 60 minutes) between active layers and ion probe solutions more than four orders of magnitude larger than the time scale for diffusion of cesium in active layers; using conservative values of 200 nm for the length scale of diffusion, and 10^{-13} m²/s for the diffusion coefficient of cesium in the active layer [47], we calculated a time scale of diffusion in the order of 0.1 s. Experimental data confirming that silver diffuses throughout the entire active layer was

provided in a previous study [32] in which the concentration of silver in ion-probed membrane samples was quantified both at the near-surface region (i.e., top $\approx 5\text{nm}$) and as an average throughout the entire active layer. The results indicated that for four membranes, including the ESPA3 membrane tested in the present study, the concentration of ion probe in the top 5 nm was the same as the average concentration throughout the active layer. For two other membranes this was not the case, but as the sample preparation procedure was the same for all six membranes, the difference was attributed to a higher concentration of ionizable carboxylic groups in the near surface region as initially proposed by other researchers [1, 25, 48].

2.7. Ion probing with silver ion (Ag^+)

Extensive details on the ion probing+RBS method for quantification of charge density in active layers can be found elsewhere [23, 49]. In brief, the negative sites in the active layers of $2.5 \times 5\text{ cm}^2$ membrane coupons were probed with Ag^+ by immersion of the membrane sample in concentrated (2×10^{-6} - 10^{-5} M) AgNO_3 aqueous solution at the pH of interest, and subsequent rinsing of the membrane sample with dilute (10^{-6} M) AgNO_3 aqueous solution at the same pH. The rinsing step ensures that the concentration of Ag^+ in the active layer not ionically associated with the

negative sites is below the detection limit of the RBS technique (~ 0.001 M for silver). Given that each silver ion detected is associated with a negative site, the measured concentration of silver in the active layer is equal to that of negative sites in the active layer. Ion probing of ESPA3 membrane samples with Ag^+ for subsequent RBS analyses was performed with silver solutions at pH values of 6.19, 8.45 and 10.50.

2.8. RBS Analyses

RBS experimental procedures and data analysis were similar to those described elsewhere [49-51]. RBS analyses were performed using a 2-MeV He^{2+} square beam with a side of 3 mm generated with a tandem Van de Graaff accelerator and a 2-MeV circular He^+ beam with a diameter of 3 mm generated with a Van de Graaff accelerator. The area analyzed for each sample was $\approx 8 \text{ cm}^2$. The incident, exit and scattering angles of the helium beam were 22.5° , 42.5° and 160° , respectively, for the square He^{2+} beam, and 22.5° , 52.5° and 150° , respectively, for the circular He^+ beam. The commercial software SIMNRA [52] was used for raw data analysis.

2.9. EDS Analyses

Energy dispersive X-ray spectroscopy (EDS) analyses were performed using a Helios NANOLAB DUALBEAM system (FEI, Hillsboro, OR) equipped

with an INCA X-ray microanalysis system (OXFORD Instruments, United Kingdom) having a Si(Li) INCA PentaFET-x3 detector. An accelerating voltage and current of 20 kV and 0.34 nA, respectively, were used. All samples were coated with 2 nm of Au/Pd to prevent charging.

3. Results and Discussion

3.1. Evaluation of the extent of dissolution and of the importance of complete dissolution of the polysulfone support in AL+sensor samples

We evaluated the extent of polysulfone dissolution by the active layer isolation procedure using energy dispersive X-ray spectroscopy (EDS) analyses of an active layer isolated on a silicon wafer. The EDS results showed that sulfur was below detection limit, therefore confirming the successful dissolution of polysulfone. Next, we evaluated the importance of ensuring the complete dissolution of the polysulfone support by comparing the cation adsorption capacity of the polysulfone support to the cation exchange capacity of the active layer. A negligible cation adsorption capacity of the polysulfone support would indicate that traces of polysulfone in a AL+sensor sample would have a negligible effect on the mass of cesium ion that associates with the AL+sensor sample, and therefore on charge density measurements.

We measured the cation adsorption capacity of the polysulfone support and cation exchange capacity of the active layer in the pH range of 6.19-10.50 using the silver probing+RBS method [23]. For the tests, we used TFC ESPA3 membrane samples that had not been subjected to the active layer isolation procedure. Figure 2 shows an illustrative RBS spectrum of a TFC ESPA3 membrane sample probed with silver at pH = 10.50. The inset in the figure zooms in on the silver signals from the active layer (*i.e.*, peak centered at ≈ 1.7 MeV) and polysulfone support (*i.e.*, plateau to the left of the 1.7 MeV peak). The silver signal counts are directly proportional to the silver content which for the case of the spectrum in Figure 2 was found to be 3×10^{-5} atom/atom in the polysulfone support and $139 \pm 2 \times 10^{-5}$ atom/atom in the active layer.

Figure 2. Rutherford backscattering spectrometry (RBS) spectrum of a TFC ESPA3 membrane sample probed with silver ion (Ag^+) at pH = 10.50. The average elemental composition of the protonated polyamide

active layer and polysulfone support were $C_{0.489}N_{0.082}O_{0.096}Cl_{0.007}H_{0.326}$ and $C_{0.500}S_{0.019}O_{0.074}H_{0.407}$, respectively.

Even though there are no negative charges in the polymer structure of polysulfone [1], RBS analyses detected a minimal but quantifiable cation uptake by the polysulfone support, likely due to non-specific adsorption. In the pH range tested (6.19-10.50), the cation adsorption capacity of the polysulfone support was 29-178 times lower in an atom/atom basis than the ion exchange capacity of the active layer. The results indicate that even if 10% of the polymer mass in the AL+sensor sample were due to undissolved polysulfone support, the error in the estimation of the areal negative charge density (sites/nm²) of the active layer in an AL+sensor sample would be negligible (<0.38%). As a result, we conclude that undissolved polysulfone residues at low percentages in AL+sensor samples do not significantly affect the measured *areal* charge density.

3.2. Suitability of AL+sensor samples for measuring mass changes via QCM analyses

Having confirmed that any traces of the polysulfone support in the AL+sensor samples are negligible, and that the ion adsorption capacity of the polysulfone support is negligible compared to the ion exchange capacity of the active layer, we proceeded to verify that AL+sensor samples were

suitable samples for measuring mass changes via QCM analyses in both air and aqueous media (*i.e.*, that Equation 1 below was valid for AL+sensor samples). The principles of operation of quartz crystal microbalances are extensively described elsewhere [34-36]. In brief, the increase/decrease in the mass (Δm) of the quartz crystal sensor (*e.g.*, mass increase due to isolation of a membrane active layer on the sensor, absorption or desorption of ion probes in the active layer) is quantified via the measurement of the decrease/increase of the resonant frequency (Δf) of vibration of the crystal sensor under an applied oscillating electric field [34-36]. If the mass added to the sensor is evenly distributed over the sensor, is significantly smaller than the mass of the sensor, does not deform internally due to oscillatory motion (*i.e.*, it is rigid), and is firmly attached to the sensor, then there is a linear relationship between Δm and Δf as expressed by the Sauerbrey equation [35, 36, 53]

$$\Delta m = -\frac{C}{n} \Delta f, \quad (1)$$

where C is the mass sensitivity constant of the quartz crystal microbalance ($C = 17.7 \text{ ng/cm}^2/\text{Hz}$ at 5 MHz), n is the overtone number, and $\Delta f/n$ is independent of n . We evaluated the suitability of the AL+sensor samples for

QCM analyses by calculating $\Delta f/n$ at overtones $n = 3, 5, 7$ and 9 , and verifying that $\Delta f/n$ was independent of n [35, 36, 53].

Figure 3 presents representative $\Delta f/n$ values for QCM sensors in water due to coating with active layers of TFC and TFN membranes. The results indicate that $\Delta f/n$ values were independent of overtone number with relative standard deviations among overtones of 1.9% and 0.8% for isolated active layers of TFC membranes and TFN membranes, respectively. The $\Delta f/n$ values were also highly stable as a function of time with relative standard deviations of less than 0.3% for frequency readings taken every 10 seconds over 15 minute periods, which indicates that the isolated active layers were firmly attached to the sensors. We observed the same lack of dependence of $\Delta f/n$ values on overtone number, and similar relative standard deviations among overtones and as a function of time for samples tested in air and for samples tested first in ultrapure water and then in ion-probe solutions (data not shown). Accordingly, we conclude that the AL+sensor samples are suitable samples for measuring mass changes in air and aqueous media via QCM analysis. Given that $\Delta f/n$ values were independent of overtone number, throughout this study we used the data for the third overtone to calculate mass changes during QCM analyses.

Figure 3. Change in frequency of vibration per overtone number ($\Delta f/n$) for QCM sensors in water due to isolation of active layers of TFC ESPA3 and TFN membranes on the sensors. The active layer of the TFN membrane consisted of 0.76%w/w LTA zeolite nanoparticles in a fully aromatic polyamide matrix. The reference value of $\Delta f/n = 0$ corresponds to the microbalance response to the sensors in ultrapure water before active layers were isolated on them.

3.3. Verification of integrity of active layers after polysulfone dissolution with DMF

Having confirmed that Equation 1 was valid for the study of AL+sensor samples, we used QCM analysis to verify that polysulfone dissolution with DMF had a minimal impact on the properties of isolated active layers by comparing their (1) mass and (2) charge density to corresponding values in non-isolated active layers (*i.e.*, in membrane samples as received from the manufacturer). In this section we discuss the mass results; the charge density results are discussed in Section 3.5. For non-isolated active layers, the total analysis area was 112 cm² (14 membrane coupons) and data was

gathered using RBS analyses. For isolated active layers, the total analysis area was 4.6 cm^2 (three AL+sensor samples) and tests were performed using QCM analyses.

The results showed that the average areal masses of isolated and non-isolated active layers were $13.2 \pm 0.3 \text{ } \mu\text{g}/\text{cm}^2$ and $12.5 \pm 0.4 \text{ } \mu\text{g}/\text{cm}^2$, respectively. The 5.4% difference in areal mass is consistent with a previous study [40] that reported that the active layer mass of a non-isolated active layer was $\approx 10\%$ larger than the active layer mass of an active layer isolated by dissolving the polysulfone support with DMF. The mass difference between isolated and non-isolated samples is likely due to variability in the active layer thickness at the different locations in the membrane sheet where the samples are cut [49]. Since manufacturers specify a possible 15% uncertainty in the permeate water flow of membrane elements with respect to specifications [54-56], but only a 4% uncertainty with respect to the specified module membrane area [54-56], then the majority of the 15% uncertainty in the permeate water flow is likely due to variability in the active layer thickness. Accordingly, we conclude that the relatively small difference (5.4%) between the areal masses of isolated and non-isolated active layers indicate that polysulfone dissolution with DMF does not result in a detectable dissolution of the active layer (and by way of the analysis in

Section 3.5, nor in a change in the negative charge density). Our results, together with those of a previous study [39] that reported that the dissolution of polysulfone with DMF did not significantly affect the transport of ferro- and ferricyanide ions in a polyamide active layer, indicate that polyamide active layers isolated by dissolving the polysulfone support with DMF can be used to study the physical and chemical properties of active layers in TFC membranes.

3.4. Cesium ion (Cs^+) as cation probe for measuring charge density via QCM analyses

The ideal cation probe for quantifying negative charge density in the AL+sensor samples via QCM analyses is monovalent, with a molecular weight as high as possible to increase sensitivity of detection, with an ionic radius as small as possible to maximize accessibility to negative sites in the active layer, and with a hydration number as small as possible to minimize the potential error in the conversion of mass of cation neutralizing negative sites to corresponding moles of cations (*i.e.*, moles of negative sites).

Among the candidate alkali metals (*i.e.*, Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), cesium is the cation that best satisfies these characteristics as it has the highest molecular weight (132.91 g/mole), a non-hydrated radius (<1.7 Å [42])

smaller than the pore radii ($>2.1 \text{ \AA}$ [44-46]) in polyamide films, the lowest hydrated radius [42, 57, 58], and one of the lowest hydration numbers [58], with three of the models used to determine average hydration numbers indicating less than one water molecule of hydration [58]. Accordingly, we used Cs^+ as the ion probe to measure negative charge density in isolated active layers via QCM analyses.

3.5. Measurement of charge density in isolated active layers

In order to quantify the charge density in isolated active layers, AL+sensor samples were exposed sequentially to CsOH aqueous solution and ultrapure water with the purpose of measuring the mass of Cs^+ that associated with the negative sites in the active layers. The tests were performed in QCM flow cells to ensure complete saturation of negative sites by Cs^+ during exposure to CsOH solutions and complete release of Cs^+ by the negative sites during exposure to ultrapure water according to ion exchange theory [59]. The pH of cesium was adjusted to $\text{pH} \approx 10.5$ as previous ion probing+RBS studies [23, 24] have shown that, in general, carboxylic groups in active layers are nearly fully ($>99\%$) ionized at $\text{pH} = 10.5$.

Figure 4a shows representative frequency changes ($n=3$) as a function of time that occurred during multiple cycles of exposure of (i) a control sensor

without isolated active layer and (ii) an AL+sensor sample, to CsOH aqueous solution at pH = 10.5 (*i.e.*, Cs⁺ absorption stage) and ultrapure water (*i.e.*, Cs⁺ desorption stage). Before the first exposure to CsOH solution, the samples were exposed to ultrapure water until stable frequency readings were achieved by the microbalance. The active layer in the AL+sensor sample was that of a TFC ESPA3 membrane coupon. As observed in Figure 4a, the control sensor indicates that a change in the frequency of vibration of the sensor occurs as a result of the change in solution. This frequency change is the result of the differences in viscosities and densities between ultrapure water and the CsOH solutions [34, 35], and is therefore also experienced by the AL+sensor sample. As a result, Equation 1 was re-written as

$$\Delta m = -C \left(\frac{\Delta f}{n} \right)_{\text{net}}, \quad (2)$$

where $(\Delta f/n)_{\text{net}} = (\Delta f/n)_{\text{AL+sensor}} - (\Delta f/n)_{\text{control}}$.

As described in Section 2.5, each exposure to ultrapure water or CsOH solutions was ended when equilibrium was attained between the AL+sensor samples and the test solution as indicated by a rate of change in the measured mass lower than 0.25 ng/cm²/min, which typically occurred within

60 minutes of exposure. The last exposure to ultrapure water in Figure 4 was used to evaluate whether an extended exposure to the test solution (i.e., longer than 60 minutes) would result in a significantly different value for the calculated mass change. The calculations show that there was a difference of less than 3% between the mass release values calculated after 60 and 420 minutes of exposure to ultrapure water. The less than 3% difference cannot be conclusively ascribed to incomplete equilibrium at 60 minutes because there are other factors that may increase the mass released at extended contact times. For example, polymer relaxation may result in changes in polymer hydration [60-62], and absorption of carbon dioxide from the atmosphere may result in a slight pH decrease of the test solution and a corresponding release of cesium from the active layer. As a result, the criteria of a rate of change of mass lower than $0.25 \text{ ng/cm}^2/\text{min}$ was considered appropriate as an indicator of equilibrium between the AL+sensor samples and test solution.

Figure 4. Representative (a) frequency changes measured using a QCM and (b) mass changes in AL+sensor samples calculated using Equation 2 as a result of sequential exposure to CsOH aqueous solution at pH = 10.50 (absorption) and ultrapure water at pH = 5.87 (desorption). The isolated active layer on the AL+sensor sample corresponds to that of a TFC ESPA3 membrane and had a mass of $12,874 \pm 332$ ng/cm². The control sample in (a) corresponds to a bare QCM sensor. Absorption and desorption values represent increase and decrease, respectively, in mass.

Figure 4b shows the calculated mass changes in the isolated active layer of the AL+sensor sample during the absorption and desorption stages of each absorption-desorption cycle. In general, the mass absorbed in the first 1-2 cycles was always higher ($\approx 40\%$ or less) than the stabilized mass absorbed in cycles 3-5. Additionally, the mass absorbed during the first 1-2 cycles was higher than the corresponding mass desorbed, but they became equal to each other and reached an approximate constant value in subsequent cycles. As a result, the first two cycles generated an irreversible mass absorbed in the active layer that plateaued in subsequent cycles. The reversible nature of

the steady amount of mass absorbed and desorbed in cycles 3-5 indicates that it is the result of the absorption and desorption of Cs^+ as expected from the deprotonation and protonation, respectively, of carboxylic groups in the polyamide structure. For the experiment depicted in Figure 4, the standard deviation among the last three desorption values (i.e., 742, 733 and 755 ng/cm^2 in cycles 3, 4 and 5, respectively) was less than 2% without any clear trend of increasing or decreasing mass released with cycle number. The 2% range of variability among the masses released in cycles 3-5 was representative of experiments with other AL+sensor samples. As a result, five absorption-desorption cycles were considered sufficient to obtain an accurate estimation with an uncertainty of $\approx 2\%$ of the mass change of the AL+sensor samples as a result of the absorption and desorption of Cs^+ . The nature of the irreversible portion of the mass absorbed in cycles 1-2 was unclear, and therefore we conducted additional tests to assess its origin.

The irreversible mass absorbed could have two origins: (i) Cs^+ ions not desorbed during exposure of the AL+sensor sample to ultrapure water; and (ii) water molecules that hydrated the active layer upon ionization of carboxylic groups and became ‘trapped’ in the active layer. To test the origin of the irreversible mass absorbed, the AL+sensor sample tested in Figure 4 (which had undergone five cycles of exposure to CsOH solution at

pH $\approx$ 10.50 and ultrapure water) was dismantled from the microbalance, dried and then used to repeat the experiment depicted in Figure 4 (*i.e.*, the AL+sensor sample was again stabilized in the microbalance with ultrapure water and subjected to five additional cycles of exposure to CsOH aqueous solution at pH $\approx$ 10.50 and ultrapure water). If Cs⁺ ions were the origin of the irreversible mass, then the new experiment would result in a frequency change response markedly different from that in Figure 4 because Cs⁺ cannot be evaporated during drying, and we would therefore expect a significantly lower accumulation of irreversible mass. Conversely, if water of hydration were the origin of the irreversible mass, then the new experiment would result in a frequency change response similar to that in Figure 4 because the water of hydration would have evaporated during drying. The results demonstrated, in over 10 experiments performed with three different AL+sensor samples, that the same frequency and mass change pattern observed in Figure 4 was obtained when the experiment was repeated after drying the AL+sensor sample between experiments. As a result we concluded that (i) the irreversible mass absorbed was due to water that hydrated the active layer and (ii) the reversible mass absorbed and desorbed after the second cycle represents the areal mass of cesium ion (

$m_{Cs,areal}$) that associates with the negative charges in isolated active layers of AL+sensor samples.

There are two factors that are likely contributors to the irreversible mass of water absorbed by the active layer during the cesium absorption-desorption cycles: (i) the higher hydrophilicity of the polymer upon ionization, and (ii) the polymer relaxation that results from ionization and ion exchange processes [60-62]. Figure 4 indicates that the additional absorption of water has both an instantaneous and a gradual component. The instantaneous component is likely the combined result of the instantaneous increase in hydrophilicity upon polymer ionization and the corresponding polymer relaxation that occurs as a result of the cesium-hydrogen exchange process and the repulsive forces between ionized polymer chains. The gradual component of water absorption is evidenced by the fact that equilibrium is not instantaneous, and is likely the result of polymer relaxation which (including shrinkage) has been suggested to account for the change in water permeability in thin-film composite membranes when feed water and/or operating conditions change [60-62].

The measured $m_{Cs,areal}$ was used to calculate the negative charge density of isolated active layers on an areal (NCD_{areal}) and volumetric (NCD_{vol}) basis according to

$$NCD_{areal} = \frac{m_{Cs,areal}}{MW_{Cs}} \quad (3)$$

and

$$NCD_{vol} = NCD_{areal} \frac{\rho_{AL}}{m_{AL,areal}}, \quad (4)$$

where $m_{AL,areal}$ is the areal mass of isolated active layer polymer in the AL+sensor sample, MW_{Cs} is the molecular weight of cesium (132.91 g/mole), and ρ_{AL} is the volumetric mass density of the active layer polymer which we assume to be 1.24 g/cm³ [40]. For the experiment of Figure 4, $m_{Cs,areal}$ and $m_{AL,areal}$ were measured as 738±10 ng/cm² and 12,874±332 ng/cm², respectively, and were used in Equations 3 and 4 to calculate $NCD_{areal} = 33.4 \pm 0.5$ sites/nm² and $NCD_{vol} = 0.53 \pm 0.02$ M. We also measured the average negative charge density in 64 cm² of non-isolated active layer (*i.e.*, eight membrane coupons) using the ion probing+RBS method and obtained a value of 32.7±2.0 sites/nm² which is only 2.1% different from the 33.4±0.5 sites/nm² value measured via QCM analyses in

the 1.54 cm² AL+sensor sample of Figure 4. The consistency between QCM and RBS results indicates that the QCM method accurately quantifies charge density in active layers, and that the dissolution of the polysulfone support with DMF does not affect charge density in the polyamide films.

The areal and volumetric charge densities measured in this study were consistent with the ranges of 16-60 sites/nm² and 0.24-0.64 M measured elsewhere by the ion probing+RBS [23, 24] and uranyl cation binding [33] methods in polyamide active layers of commercial reverse osmosis and nanofiltration membranes. It is important to note that the QCM method shares with the ion probing+RBS method the advantage of providing the $m_{AL,areal}$ value that is needed in Equation 4 to characterize charge density as an intensive property (*i.e.*, charge density per unit volume, NCD_{vol} , and/or charge density per unit mass of active layer polymer, $NCD_{areal} / m_{AL,areal}$). The characterization of charge density as an extensive property (*i.e.*, charge density per unit area of membrane, NCD_{areal} , which depends on active layer thickness) does not require of the $m_{AL,areal}$ value and can be obtained using the QCM, ion probing+RBS and uranyl cation binding methods. In the remainder of this manuscript we report NCD_{areal} in units of sites/nm², and provide $m_{AL,areal}$ for easy conversion of NCD_{areal} to NCD_{vol} using Equation 4.

3.6. Repeatability of charge density measurements and resilience of AL+sensor samples

We use the term “repeatability” to refer to measurements performed on *the same AL+sensor sample under the same experimental conditions*. Figure 5 displays the repeatability of charge density measurements in the isolated active layer of a TFC membrane sample using the QCM method described above. The tests were conducted over a four-month period with an AL+sensor sample that was repeatedly mounted in the microbalance, tested, dismounted from the microbalance, rinsed, dried, stored and re-used again. The pH of cesium solutions was in the range of 10.54-10.62. The tests at days 1, 6, 25 and 131 correspond to tests 1, 2, 3 and 12, respectively, performed with the AL+sensor sample. Tests 4-11 did not correspond to charge density measurements, and thus are not reported in this manuscript. The results indicate that the average charge density of the isolated active

layer in the AL+sensor sample was 34.2 ± 1.0 sites/nm² which means that the charge density measurements were repeatable within 3% over the four-month period of measurements. The results therefore indicate that: (i) charge density measurements with the QCM method are highly repeatable; (ii) AL+sensor samples are resilient to deterioration due to handling, testing, cleaning, drying and storage; and (iii) AL+sensor samples can be used over long periods of time. The possibility of sample re-use has not been reported for the other two methods available in the literature for measuring volume-averaged charge density in active layers (*i.e.*, ion probing+RBS [23, 24] and uranyl cation binding [33]), and therefore sample re-usability and resilience represent an advantage of the QCM method.

We estimated a conservative detection limit (DL) for charge density values obtained from the cesium absorption-desorption cycles described in Section 3.5. We followed standard guidelines [63] for the determination of analytical detection limits and obtained a detection limit of 2.2 sites/nm² (49.4 ng/cm²), which is consistent with the repeatability of 1 site/nm² found above for charge density measurements performed using the same AL+sensor sample.

Figure 5. Repeatability of the negative charge density measured by QCM analyses at pH = 10.54-10.62 in an isolated active layer of the TFC ESPA3 membrane. All tests were performed with the same AL+sensor sample. The mass of the isolated active layer was $13,211 \pm 319$ ng/cm².

3.7. Effect of cesium concentration on charge density measurements

We verified that the mass increase detected by the QCM was due to Cs⁺ neutralizing negative sites and not due to solute (*i.e.*, CsOH, CsCl) partitioning into the active layer [64, 65]. We did this by confirming that under our experimental conditions of cesium concentration in solution (1 mM), the partitioning of cesium into the active layer was not detected by the microbalance. The tests consisted of measuring charge density at pH $\approx$ 10.5 in the isolated active layer of an AL+sensor sample using the procedures described above, but varying the cesium concentration in the ion probe CsOH solution by 300% (1-3 mM) via addition of a cesium salt (CsCl) in the range of 0-2 mM. Since increasing the pH of the cesium solutions to pH

≈ 10.5 required a final CsOH concentration of ≈ 1 mM, the background CsCl concentrations tested of 0, 0.5, 1.0 and 2.0 mM corresponded to cesium concentrations of approximately 1.0, 1.5, 2.0 and 3.0 mM, respectively. As described extensively in the literature [19, 66], the partitioning of solutes is proportional to their concentration in solution. As a result, if solute partitioning accounted for a significant fraction of the mass change in the active layer detected by the QCM, then changing the cesium (salt) concentration in the ion probe solution would produce a significant variation in the mass change detected by the QCM. The results, presented in Figure 6, indicate that the relative difference between the charge densities measured at the maximum (3 mM) and minimum (1 mM) cesium concentrations in solution was only 3.8%; this level of variability is comparable to the repeatability (3%) obtained in Section 3.6 for the negative charge density in the same AL+sensor sample at a cesium concentration in solution of 1 mM. Given that a 300% difference in cesium concentration in solution resulted in less than 4% variability in the QCM response, we concluded that the measured masses absorbed and released by the AL+sensor samples were due to Cs^+ attachment and detachment from negative sites in the isolated active layer, and not to solute partitioning.

Figure 6. Effect of cesium concentration in solution on the negative charge density measured by QCM analyses at pH = 10.48-10.54 in an isolated active layer of the TFC ESPA3 membrane. The background CsCl concentrations of the solutions with cesium concentrations of 1, 1.5, 2.0 and 3.0 mM were 0, 0.5, 1.0 and 2.0 mM, respectively. In all cases, the pH was adjusted adding CsOH to a concentration of ≈ 1 mM. The mass of the isolated active layer was $13,211 \pm 319$ ng/cm².

3.8. Reproducibility of AL+sensor sample preparation and analysis

Figure 7 shows the areal and volumetric negative charge density measured for three different AL+sensor samples of the TFC ESPA3 membrane. The three samples were prepared using membrane coupons from within a relatively small (20×20 cm²) region of the flat sheet ESPA3 membrane. The pH of CsOH solutions was in the range of 10.54-10.60, and no background CsCl was used. The results indicate that there was a variability of 2.0%, 3.9% and 2.3% in the mass of active layer isolated, areal negative charge density and volumetric negative charge density, respectively. The 3.9% variability of the areal negative charge density among the three samples

tested was similar to the 3% variability obtained above for repetitive measurements of charge density in a single AL+sensor sample under the same experimental conditions. The results therefore demonstrate that the procedures described in this study for active layer isolation and quantification of charge density in active layers are highly reproducible.

Figure 7. Variability in the negative charge density measured by QCM analyses at pH = 10.54-10.60 among three different isolated active layers of the TFC ESPA3 membrane. In all cases, the pH was adjusted using CsOH, no background CsCl was used, and the results correspond to the first test performed after active layer isolation. The masses of isolated active layer in AL+sensor samples 1, 2 and 3 were $13,211 \pm 319$ ng/cm², $12,874 \pm 332$ ng/cm² and $13,528 \pm 221$ ng/cm², respectively.

3.9. Comparison between the ionization behaviors of TFC and TFN active layers

Figure 8 presents measurements of negative charge density as a function of pH for (a) the TFC ESPA3 membrane and (b) a TFN membrane. The zeolite nanoparticle content in the aromatic polyamide active layer of the TFN

membrane was 0.76%w/w, which is above the zeolite contents that have been documented [15, 18, 67] to result in water flux enhancement. The mass of active layer isolated on each of the two TFC AL+sensor samples tested was $\approx 35\%$ higher than the corresponding mass on the TFN AL+sensor sample. As a result, the charge densities are presented in molar units in order to facilitate the comparison of TFC and TFN results. Figure 8 shows that the QCM method was able to detect the changes in negative charge density that occurred as a function of pH in both the TFC and TFN samples. The negative charge density of the active layer of the TFC membrane was also measured at three different pH values using the silver probing+RBS method to confirm the validity of the QCM results. The total analysis area for QCM data points was 3.01 cm^2 (two AL+sensor samples), and the corresponding area for RBS data points was 24 cm^2 (three membrane coupons) except for the data at $\text{pH} = 10.5$ for which the total analysis area was 64 cm^2 (eight membrane coupons). The results presented in Figure 8a show that QCM and RBS results were in agreement, and therefore that the QCM method can be used to study the ionization behavior of the active layers of TFC and TFN membranes. Since previous studies [32] already confirmed that silver ion probes diffuse throughout the entire active layer, the matching RBS and QCM results confirmed that the cesium ion probes

also diffused throughout the entire active layer in the QCM procedure. The results also demonstrate one advantage of the re-usability of AL+sensor samples: one single AL+sensor sample can be used to study the ionization behavior of the active layer as a function of pH.

Figure 8. Negative charge density in isolated active layers as a function of pH. (a) Ionization behavior of the TFC ESPA3 active layer measured using the QCM and silver probing+RBS methods. The masses of isolated active layer on the two AL+sensor samples tested were

13,211±319 and 13,528±221 ng/cm²; error bars for the QCM data points are <5% of the corresponding charge density. Error bars for the RBS data points correspond to variability among three samples for tests at pH = 6.19 and 8.45, and among eight samples for tests at pH = 10.50. (b) Ionization behavior of a TFN active layer measured using the QCM method for which data points correspond to tests with an AL+sensor sample with a mass of isolated active layer of 9,839±220 ng/cm².

We modeled the ionization behavior of the TFC and TFN active layers assuming acid-base equilibrium between the ionizable sites in the active layers and the ion-probe solutions as given by [23, 24]

$$\text{NCD} = \text{NCD}_T \sum_{i=1}^n \left(w_i \frac{10^{-\text{p}K_{a,i}}}{10^{-\text{pH}} + 10^{-\text{p}K_{a,i}}} \right), \quad (5)$$

where NCD is the negative charge density at any given pH, NCD_T is the negative charge density at full ionization, and w_i is the fraction of ionizable sites having $\text{p}K_a = \text{p}K_{a,i}$ where $\sum_{i=1}^n w_i = 1$. The fitting results in Figure 8 indicate that not one but two $\text{p}K_a$ values were required to describe the ionization behavior of each the TFC and TFN active layers. Fitted values for the TFC membrane were NCD_T = 0.54±0.03 M, $\text{p}K_{a,1}$ = 5.74±1.06, $\text{p}K_{a,2}$ = 8.26±0.27 and w_1 = 0.31±0.14. Corresponding values for the TFN membrane were NCD_T = 0.49±0.01 M, $\text{p}K_{a,1}$ = 5.34±0.06, $\text{p}K_{a,2}$ = 8.97±0.04 and w_1 = 0.33±0.01.

While we could not find studies reporting measurements of charge density in active layers of TFN membranes, the bimodal pK_a distribution that we obtained for both the TFC and TFN membranes is consistent with previous studies [23-25, 32, 33] in which the ionization behavior of the TFC active layers tested could not be described by unimodal pK_a distributions. Previous studies [24], however, showed that samples of the ESPA3 membrane had a pK_a distribution in which the majority ($92\pm 7\%$) of ionizable sites had a pK_a value of 5.86; this pK_a value fell between the $pK_{a,1} = 5.23-5.72$ and $pK_{a,2} = 8.46-9.87$ values of the other five polyamide TFC membranes studied. Even though our results for the TFC ESPA3 membrane were not dominated by one pK_a value, the fitted pK_a values also fell between the $pK_{a,1}$ and $pK_{a,2}$ values mentioned above.

It has been hypothesized that one reason for the reported higher water flux of TFN membranes compared to their TFC counterparts may be a lower degree of polymerization and crosslinking of the polyamide matrix in the TFN membrane as a result of the presence of the nanoparticles [18]. If this were the case, TFN membranes would have a larger negative charge density than TFC membranes because in aromatic polyamides a lower degree of polymerization results in a higher concentration of carboxylic groups [1]. In contrast, we obtained that the NCD_T for the TFN active layer (0.49 ± 0.01 M)

was within the range of values (0.24-0.64 M) previously reported [24] for several aromatic TFC membranes, and only 2-10% lower than the NCD_T values for several reverse osmosis membranes (see Ref [24] and the NCD_T (0.54 ± 0.03 M) for the TFC samples in Figure 8). Furthermore the $\text{p}K_{a,1}$ and $\text{p}K_{a,2}$ values fitted for the TFN data were consistent with the reported [24] ranges for $\text{p}K_{a,1}$ and $\text{p}K_{a,2}$ values mentioned above for TFC active layers. Accordingly, our results indicate that the charge density, ionization behavior of carboxylic groups and degree of crosslinking of the polyamide matrix in the specific TFN active layer sample tested in this study is not significantly different from those of TFC active layers.

One possible factor that may contribute to the higher water permeability of TFN membranes is thinner active layers. Assuming an active layer mass density of 1.24 g/cm^3 [40], we calculated an average thickness of $\approx 79 \text{ nm}$ and $\approx 108 \text{ nm}$ for the active layers of the TFN and TFC membranes, respectively, tested in Figure 8. The TFN thickness of $\approx 79 \text{ nm}$ is between the two lowest thicknesses (i.e., 72 nm and 87 nm) obtained in an RBS study [24] of a group of six TFC aromatic polyamide active layers where the membranes with the two lowest and two highest thicknesses were nanofiltration and reverse osmosis membranes, respectively. Accordingly,

the relatively thin active layer of the TFN membrane sample suggests that active layer thickness may play a role in the reported [18] higher water permeability observed for TFN membranes as compared to corresponding TFC membranes. To test this hypothesis, a systematic study of how the inclusion of nanoparticles in polyamide active layers affects the physico-chemical properties of the active layer (e.g., thickness, degree of polymerization, etc.), and how the changes in these properties affect membrane performance, is required.

4. Conclusions

We demonstrated that the negative charge density in the active layers of thin-film composite (TFC) and thin-film nanocomposite (TFN) membranes can be accurately quantified as a function of pH by measuring, with a quartz crystal microbalance (QCM), the mass of cesium ion that associates with charged sites in an active layer isolated on a QCM sensor. Our results indicate that charge density measurements with the QCM method are repeatable, reproducible, and accurate, and that active layers isolated on QCM sensors are resilient to deterioration due to handling, QCM testing, cleaning, drying and storage, and can be used for extended periods of time. We used the QCM method to characterize a zeolite TFN membrane having

an active layer with an aromatic polyamide matrix and found that the ionization behavior of the active layer was similar to that of polyamide active layers of TFC membranes tested in this study and in the literature.

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Figure 1. Schematic of the procedure used for the isolation of active layers of thin-film composite (TFC) and thin-film nanocomposite (TFN) membranes on quartz crystal microbalance (QCM) sensors and silicon wafers. (a) The polyester backing is peeled off from the active layer and polysulfone support. (b) The membrane coupon minus polyester backing is placed against the QCM sensor with the active layer facing the sensor. (b-c) The membrane coupon and sensor are secured to each other using a custom stainless steel (SS) 316 assembly, and (c) the polysulfone support is dissolved using dimethylformamide (DMF). (d) The final product is the isolated active layer on the QCM sensor (AL+sensor sample).

Figure 2. Rutherford backscattering spectrometry (RBS) spectrum of a TFC ESPA3 membrane sample probed with silver ion (Ag^+) at pH = 10.50. The average elemental composition of the protonated polyamide active layer and polysulfone support were $\text{C}_{0.489}\text{N}_{0.082}\text{O}_{0.096}\text{Cl}_{0.007}\text{H}_{0.326}$ and $\text{C}_{0.500}\text{S}_{0.019}\text{O}_{0.074}\text{H}_{0.407}$, respectively.

Figure 3. Change in frequency of vibration per overtone number ($\Delta f/n$) for QCM sensors in water due to isolation of active layers of TFC ESPA3 and TFN membranes on the sensors. The active layer of the TFN membrane consisted of 0.76%w/w LTA zeolite nanoparticles in a fully aromatic

polyamide matrix. The reference value of $\Delta f/n = 0$ corresponds to the microbalance response to the sensors in ultrapure water before active layers were isolated on them.

Figure 4. Representative (a) frequency changes measured using a QCM and (b) mass changes in AL+sensor samples calculated using Equation 2 as a result of sequential exposure to CsOH aqueous solution at pH = 10.50 (absorption) and ultrapure water at pH = 5.87 (desorption). The isolated active layer on the AL+sensor sample corresponds to that of a TFC ESPA3 membrane and had a mass of $12,874 \pm 332 \text{ ng/cm}^2$. The control sample in (a) corresponds to a bare QCM sensor. Absorption and desorption values represent increase and decrease, respectively, in mass.

Figure 5. Repeatability of the negative charge density measured by QCM analyses at pH = 10.54-10.62 in an isolated active layer of the TFC ESPA3 membrane. All tests were performed with the same AL+sensor sample. The mass of the isolated active layer was $13,211 \pm 319 \text{ ng/cm}^2$.

Figure 6. Effect of cesium concentration in solution on the negative charge density measured by QCM analyses at pH = 10.48-10.54 in an isolated active layer of the TFC ESPA3 membrane. The background CsCl concentrations of the solutions with cesium concentrations of 1, 1.5, 2.0 and

3.0 mM were 0, 0.5, 1.0 and 2.0 mM, respectively. In all cases, the pH was adjusted adding CsOH to a concentration of ≈ 1 mM. The mass of the isolated active layer was $13,211 \pm 319$ ng/cm².

Figure 7. Variability in the negative charge density measured by QCM analyses at pH = 10.54-10.60 among three different isolated active layers of the TFC ESPA3 membrane. In all cases, the pH was adjusted using CsOH, no background CsCl was used, and the results correspond to the first test performed after active layer isolation. The masses of isolated active layer in AL+sensor samples 1, 2 and 3 were $13,211 \pm 319$ ng/cm², $12,874 \pm 332$ ng/cm² and $13,528 \pm 221$ ng/cm², respectively.

Figure 8. Negative charge density in isolated active layers as a function of pH. (a) Ionization behavior of the TFC ESPA3 active layer measured using the QCM and silver probing+RBS methods. The masses of isolated active layer on the two AL+sensor samples tested were $13,211 \pm 319$ and $13,528 \pm 221$ ng/cm²; error bars for the QCM data points are <5% of the corresponding charge density. Error bars for the RBS data points correspond to variability among three samples for tests at pH = 6.19 and 8.45, and among eight samples for tests at pH = 10.50. (b) Ionization behavior of a TFN active layer measured using the QCM method for which

data points correspond to tests with an AL+sensor sample with a mass of isolated active layer of $9,839 \pm 220 \text{ ng/cm}^2$.

Highlights

- A method was developed to measure charge density in thin-film membranes
- Charged sites in active layers are probed with cesium ion
- The cesium mass in the active layer is measured with a quartz crystal microbalance
- The method is a reliable, user-friendly, bench-top method
- Thin-film composites and nanocomposites tested had similar ionization behaviors

Active layers on microbalance sensors

Figure 1

Figure 2

Figure 3

Figure 4

Figure 7

Figure 3-BW

Figure 4-BW