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Optical Properties and Swelling of Thin Film Perfluorinated Sulfonic-Acid Ionomer

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Perfluorinated sulfonic-acid (PFSA) ionomers are members of a class of ion-conductive polymers that are commonly used in both membranes and catalyst layers in polymer-electrolyte fuel cells. Transport properties of thin film ionomers and their deviation from bulk properties are still unclear. Label-free, high-speed Surface Plasmon Resonance imaging (SPRi) is proposed to simultaneously measure refractive index and thickness of a 30 nm thick Nafion film at relative humidity of 3%, 36%, and 93%. The result shows the thickness of the thin film increases with increasing the relative humidity. The refractive index of the thin Nafion film decreases from 1.310±0.003 to 1.228±0.003 when the relative humidity increases from 3% to 93%. The drop in optical properties of 30 nm thick Nafion film, indicates the void part of hydrated Nafion film is filled with a mixture of water and water vapor.

Introduction

Perflurosulfanic acid ionomers like Nafion are the standard materials used in the membrane/or catalyst layers for fuel cells and other electrochemical devices (1). Numerous studies have been undertaken to understand how the structure of Nafion and its water uptake affect the material properties and the performance of fuel cell (2, 3). This database of information is associated with the water sorption of Nafion membrane with the thickness of 1 to 200 μm, but the properties of Nafion thin films (< 1μm) are relatively unmapped (4, 5). It is known that thin film confinement affects the hydration behavior of thin Nafion film (4). Recently, Quartz-crystal microbalance (6, 7), SPRi (8), spectroscopic ellipsometry (6, 7, 9, 10), grazing-incidence x-ray scattering (6), and neutron reflectivity (7, 11) are used to study water sorption of thin Nafion film at different relative humidity (RH) levels.

Among these methods, spectroscopic ellipsometry has been used as the main method in characterizing the thin polymer film properties such as optical properties and thickness (12). However, spectroscopic ellipsometry cannot simultaneously measure the thickness and optical properties of a thin film below a threshold thickness. There is not a united value mentioned for the threshold thickness in the literatures; thickness of 30 nm (12), 15 nm (13), and 10 nm (14) are reported. Below this threshold, the refractive index and thickness cause very similar changes in the measured ellipsometry parameters. Consequently, refractive index cannot be separated from the thickness. A general solution for this limitation is to assume a known refractive index and measure the thickness of a nm-thin film. Moreover, substrate or ionomers roughness can cause uncertainty in the measurement using ellipsometry technique (9). On the other hand, characterization techniques such as ellipsometry, grazing-incidence x-ray scattering, and neutron reflectivity have temporal resolutions of more than 10 minutes, which can limit their applications in the real-time visualization of water-uptakes in thin ionomers films (15). Therefore, there is a need for a visualization technique to help with characterizing transport properties of thin ionomers film especially samples with thicknesses smaller than 30 nm.

SPRi is a label-free surface monitoring technique that is sensitive to the optical thickness, i.e. the product of film thickness and local index of refraction, of a dielectric test medium located within a few hundred nanometers near a solid surface. The SPRi system includes an illumination system, optical arrays to make chromatic p-polarized collimated light, sensing apparatus includes prism/gold coated glass/test medium, and a CCD camera to record images. When p-polarized light is launched at the interface of a prism and gold through the attenuated total internal reflection, it transfers part of its energy to excite free electrons. The incident angle at which the intensity of reflected light is minimum is called surface plasmon resonance (SPR) angle. The SPR angle contains useful information, such as optical thickness of a test media.

Similar to spectroscopic ellipsometry, independent detection of refractive index and thickness is challenging using SPRi for thin films with thicknesses smaller than 30 nm. Below the threshold thickness, changes in the refractive index of a film causes very small variation in SPR angle, which is beyond the angular resolution of commercial SPRi system or manual SPRi system. As an example, when 10 nm film exists on a 50 nm gold surface, the SPR angle at the wavelength of 600 nm changes from 45.55º to 45.60º while the refractive index changes from 1.30 to 1.31. Recently, we developed an automated SPRi system capable of angular scanning up to 0.001 degree. We showed the developed automated SPRi system can measure near-field fluidics transport phenomena at high lateral resolution (4 μm) and temporal resolution (up to 10,00 frame per second) (16, 17). In this work, automated SPRi is implemented to measure the thickness and optical properties of a Nafion film with the thickness of 30 nm at different relative humidity levels (of 3%, 36%, and 93%).

Experimental Methods

Automated SPRi System

Figure 1 shows the schematic of the automated SPRi system. Light from an LED illumination system passes through an optical array to make a p-polarized collimated light. To create a monochromatic light, a bandpass filter with the full width at half maximum of 10 nm was placed after the optical arrays. The light directed to the prism by passing through stationary and rotating mirrors. The reflected light from the prism is guided to the camera by implementing another set of stationary and rotating mirrors. The combination of motorized rotary stages and motorized linear stages enables SPRi with angular modulation (AM) at high angular resolution (~ 0.001 to 1 degree). The result from SPRi with AM can provide a reflectance curve of a thin film at a fixed wavelength. The reflectance curve has the SPR angle that can be used for the measurement of refractive index and thickness of an ionomer thin film. More details about SPRi and automated SPRi can be found in our recent work (16).

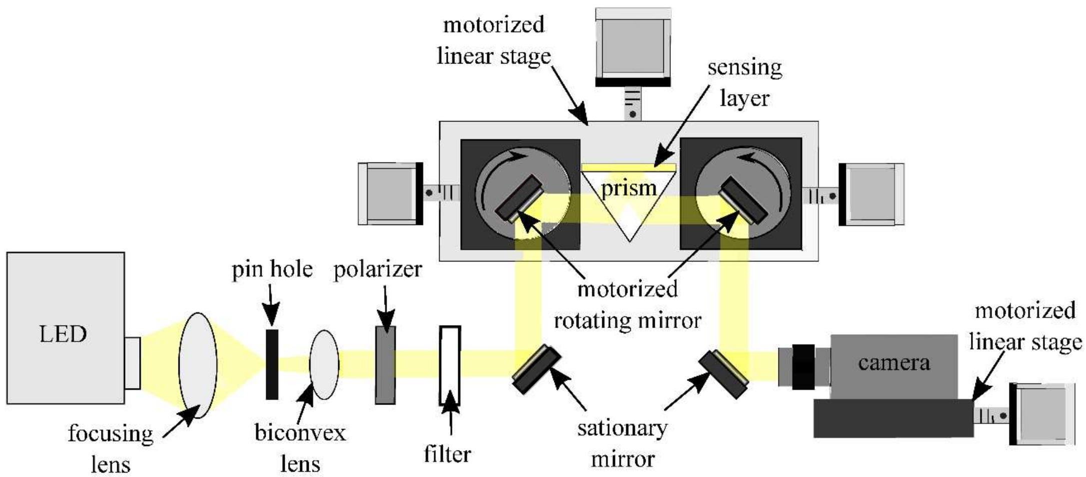


Figure 1. Schematic of automated SPRi system.

Sample Preparation

Aluminosilicate glass slide (size of 25 mm×75 mm×0.7 mm) with 50 nm of gold over 2.5 nm titanium adhesion layer was purchased from Platypus Technologies Llc, USA. To prepare the thin PFSA ionomer film, Nafion EW1100 ionomer solution was spin coated on the gold coated glass. The sample preparation was done at the Lawrence Berkley National laboratory. After the coating, the Nafion coated sample was annealed at 146 °C for 60 minutes. The fabricated ionomer film has a nominal thickness of 28-30 nm. The Nafion coated glass slide was cut to the size of 25 mm× 32.5 mm before the visualization experiment using SPRi.

Experimental Setup

The schematics of experimental setups are depicted in Figure 2. The Nafion coated glass was placed above the prism using an index matching liquid with a refractive index of 1.52 at the wavelength of 589 nm. A simple enclosure was built from acrylic plexiglass to sustain an environmental condition at different relative humidity levels. A PDMS film of thickness ~ 5 mm is used to seal the enclosure. The testing setup including enclosure, Nafion coated glass, and prism was clamped. A DHT22 humidity (resolution of 0.1% RH) and temperature (resolution of 0.1 ºC) sensor was connected to the Arduino Mega controller to read the temperature and relative humidity inside the chamber. Dry nitrogen gas was supplied to the enclosure to minimize the relative humidity above the ionomer sample, Figure 1(a). The relative humidity of 3% and temperature of ~25 ºC was achieved with this setup. The sample kept in this condition for more than 3 hours to ensure the Nafion film reaching an equilibrium condition. AM SPRi with a mirror rotation increment of 0.1 degree was used with three wavelengths of 600 nm, 640 nm, and 680 nm to find the refractive index and thickness of the sample. At each wavelength, the SPRi with AM was repeated two to three times to ensure the repeatability of the result. The same experimental protocol was repeated at the ambient condition –36 % RH– for characterization of Nafion film properties. To increase the relative humidity inside the enclosure, the nitrogen gas was passed through water before entering the enclosure, Figure 2 (b). The relative humidity of 93% was yielded in this state. The same experimental procedure was repeated to measure the Nafion film properties. These three environmental conditions were used for studying the behavior of thin Nafion film.

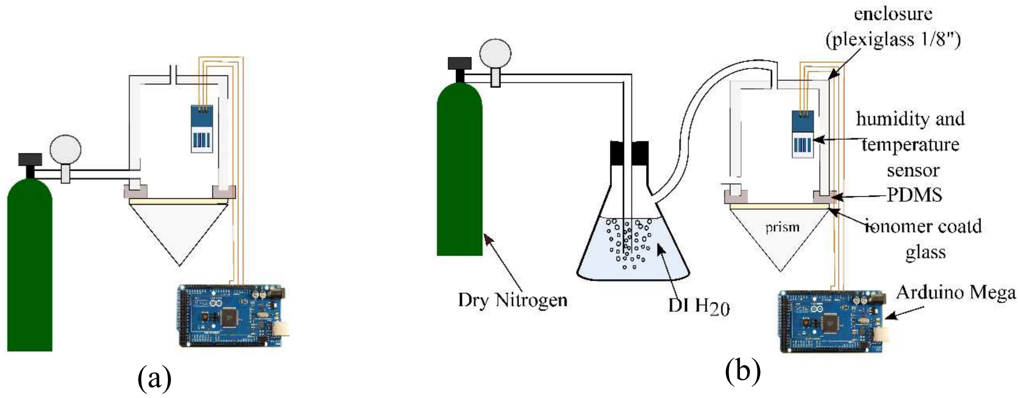


Figure 2. Schematic of experimental setup (a) at 3% RH (b) 93% RH.

Results and Discussion

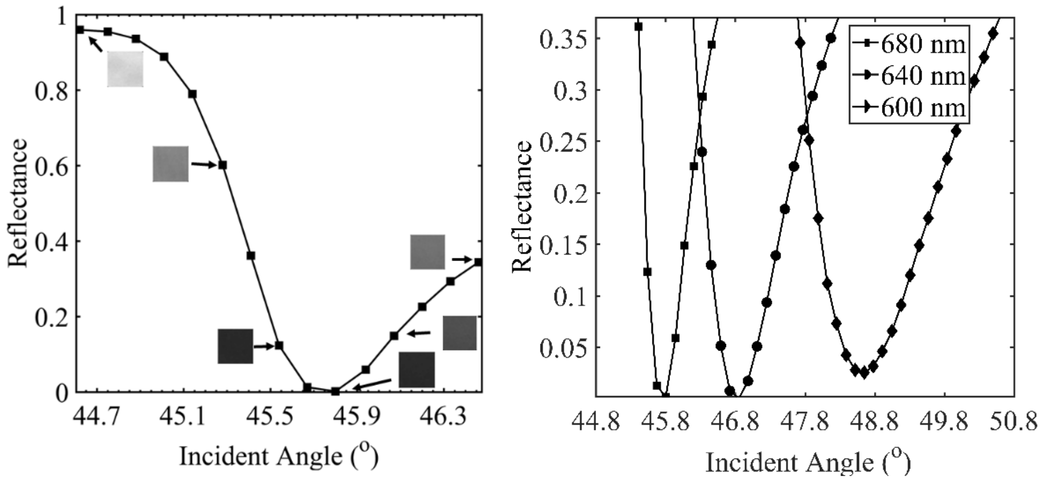
SPRi of Nafion Film and Approach of Data Fitting

SPRi with AM does not directly measure film properties such as film thickness and refractive index. It generates a reflectance curve with a SPR angle that is wavelength dependent. The difference between the refractive index of glass and index matching liquid is very small (~0.0023 at the wavelength of 589 nm) that is beyond the capability of SPRi with angular modulation to detect it. The three layers of prism, index matching liquid, glass slide can be considered as a single layer of BK7 glass. The theoretical SPR reflectance for the four-layers system –Bk7 glass, gold, Nafion, air– can be represented with a Fresnel equation (18):

$$Reflectance = \frac{r_{12}[1+exp(-2ik_2d_2)]+[r_{12}r_{23}+exp(-2ik_2d_2)]r_{34}exp(-2k_3d_3)}{1+r_{12}r_{23}exp(-2ik_2d_2)+[r_{23}+r_{12}exp(-2ik_2d_2)]r_{34}exp(-2k_3d_3)} \quad [1]$$

where r_{ij} represents the coefficient of reflection between the i^{th} and the j^{th} layers, k is the wave vector, and d is the thickness of a layer. Subscripts *1, 2, 3*, and *4* indicate the BK7 prism, gold, Nafion, and air. The thicknesses of first and last layers are considered infinite, and thickness of gold layer is 50 nm. The optical properties and thickness of all layers except Nafion film is known. The optical constant of the unknown film at each wavelength can be described by a complex number, $N=n-ik$ where n is the real part and k is the complex part of the refractive index. Studies showed the complex part of Nafion refractive index is very small (order of 0.001) and can be considered zero (9, 10). To simplify our calculation, we assume the refractive index of Nafion is fixed between wavelength of 600 nm to 680 nm; in reality, the real part of Nafion's refractive index varies less than 0.002 when the wavelength changes from 600 nm to 680 nm. To solve equation [1] with two unknowns, the experimental data of SPR angles are required to fit into the equation.

Figure 3 (a) shows the experimental reflectance curve for a 30 nm Nafion film at the 3% RH. The SPR angle for this sample occurs at 44.80º. The intensity of image at each incident angle was converted to the reflectance unit for easy comparison with theoretical result (16). Figure 3 (b) shows the reflectance curves for the 30 nm thick Nafion film at 3% RH and three wavelengths of 600 nm, 640 nm and 680 nm. The experimental data is fitted to equation [1] holding the SPR angle fixed. Multiple trials at different wavelengths provides multiple equations that allow for the simultaneous determination of both refractive index and thickness. As the experimental reflectance at each incident angle is the mean value of reflectance over ~10^6 pixels in the field of view (~1×1 cm^2), the SPRi result is independent of surface roughness.



(a) (b)

Figure 3. (a) Experimental reflectance curve for 30 nm thick Nafion film at 3% RH and wavelength of 680 nm (b) the reflectance curve of 30 nm thick Nafion film at 3% RH and three wavelengths of 600nm, 640 nm, 680 nm; the solid lines connecting the points are for ease of readability.

Nafion Film Properties at Different Relative Humidity Levels

Figure 4 shows the thickness and refractive index of a Nafion film with a nominal thickness of 28-30 nm at three relative humidity conditions. The results show the thickness of the thin film is 30 nm at close to dry condition (3% RH), confirming the baseline thickness. With increasing the relative humidity respectively to 36% and 93%, the thickness of the thin Nafion film increases to 34 nm (swelling ratio of 13%) and 41±3 nm (swelling ratio of 36±10%). The large error in our measurement originates from the resolution chosen for SPRi with AM. By decreasing the increment of angle scanning, the error in determining the accurate SPR angle reduces; Consequently, the data fitting to the theoretical model can be implemented with higher precision. The swelling ratio measured from our work is two to four times larger than the swelling ratio of thin Nafion film reported in other studies. Petrina (2013) measured swelling of 29.7 nm thick Nafion film on a 50 nm gold with 2.5 titanium adhesion layer using ellipsometry. The 29.7 nm thick Nafion film swells ~10% when relative humidity reaches to ~93%. Kusoglu et al (2014) studied the effect of sample preparation on swelling of 25 nm thick Nafion film coated on a 50 nm gold with 20 nm chromium. Their result shows the swelling ratio of ~8-10% occurs when relative humidity reaches 100 %. The huge difference in swelling ratio of our work compares to the other works can be related to the effect of substrate and processing. Moreover, the refractive index of Nafion film in this work at the relative humidity of 3% is 1.310±0.002 which is less than the refractive index of Nafion, 1.34-1.38, in other studies (6, 10). As the refractive index has a direct relationship with density, the larger swelling ratio in our work could be attributed to the weaker intermolecular bond in the ionomer structure.

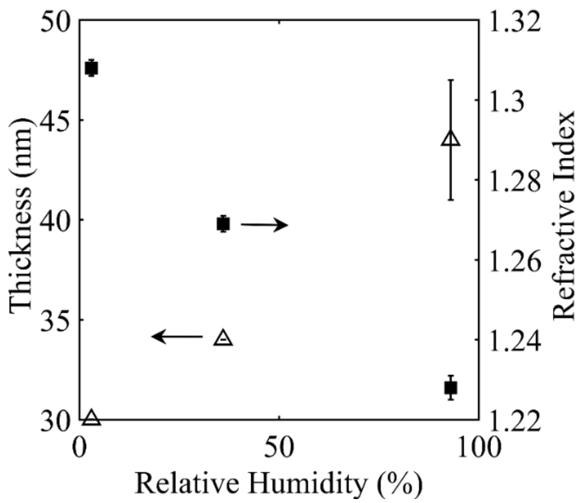


Figure 4. The effect of relative humidity on refractive inex and thickness of 30 nm thick Nafion film.

The smaller refractive index of ionomers has been reported for Nafion films with the thicknesses less than 30 nm (9, 10). With increasing the relative humidity to 36% and 93% in our experiment, the refractive index of thin Nafion film decreases to 1.269±0.002 and 1.228±0.003. The decrease in the refractive index of confined ionomer film due to the increase in relative humidity has been reported in other studies (10, 19). Petrina (2013) observed the refractive index of confined 70 nm thick Nafion film on SiO_2 substrate decreases from 1.338 at 0% RH to 1.327 at 95% RH which is lower than the refractive index of water (10). Other studies reported refractive index of Nafion generally decreases from 1.34-1.38 (dry condition) and approaches to 1.33, refractive index of water; studies mentioned changes in the refractive index is the result of the change in density of film and addition of water, which has a lower refractive index, in the structure of swollen film (19)

When the refractive index of ionomer is less than 1.33 such as the sample used in our work, the adsorption of water must increase the refractive index. Therefore, the change of refractive index from 1.310±0.002 to the smaller values such as 1.269±0.002 and 1.228±0.003 could indicate other scenarios like changes in the density of ionomer film and the presence of materials with the lower refractive index such as water vapor, nitrogen, or air rather than just liquid water in the structure of swollen Nafion film. Hence, as the film swells, there is a possibility of void space (air/water vapor) creation in the porous ionomer matrix.

Here, the Lorentz-Lorenz equation for a complex material is used to determine the components of swollen Nafion film. The structure of Nafion film is assumed to consist of ionomer part and void part. It is assumed the volume and refractive index of ionomer is constant during the swelling. The void volume is the increase in the volume of the thin film due to swelling; the void part can be filled with water, water vapor/air/nitrogen. The effective refractive index of a swollen ionomers film can be calculated from the volume fraction and refractive index of each component (20):

$$\frac{n_{eff}^2-1}{n_{eff}^2+2}=\frac{d_{void}}{d_{void}+d_{ionomer}}\left(\frac{n_{void}^2-1}{n_{void}^2+2}\right)+\frac{d_{ionomer}}{d_{void}+d_{ionomer}}\left(\frac{n_{ionomer}^2-1}{n_{ionomer}^2+2}\right) \quad [2]$$

where, $n_{ionomer}$, n_{void}, and n_{eff} are respectively the refractive indices of ionomer, void part, and the effective refractive index. The $d_{ionomer}$ and d_{void} are respectively the thickness of polymer and the thickness of the void part. The properties of thin Nafion film at 3% RH were used as the baseline ($n_{ionomer}$=1.308 and $d_{ionomer}$=30 nm). The value used for n_{eff} is the refractive index measured from the experiment, Figure 4. The n_{void} can be calculated by applying the known parameters into equation [2] at 36% RH and 93% RH. The result shows the n_{void} at 36% RH is 1.0004 which is very close to the refractive index of water vapor/air/nitrogen (~1.000277 between the wavelengths of 600 nm to 680 nm). When the relative humidity increases to 93%, the n_{void} is 1.0591 which is significantly larger than the refractive index of the mentioned gasses. The increase in refractive index at 93% RH allows us to assume that the void space is now partially filled with water liquid. With the assumptions that the void part is a combination of water and water vapor, and refractive index of water molecule is the same as refractive index of bulk liquid water, equation [2] is implemented to find the volume fraction of water inside the Nafion film. The results indicate the Nafion film at 93% RH consists of ionomer, water, and water vapor with the volume fractions of 0.6818, 0.0600, and 0.2581 respectively. The result of this work shows SPRi with AM can be implemented to find the optical properties of thin PFSA ionomers. In our future works, we will use SPRI with AM and intensity modulation to study the real-time diffusion of water in the confined thin ionomers film.

Conclusion

A 30 nm thick Nafion film prepared by spin coating of Nafion EW1100 on the gold substrate was examined for physical properties using SPRi with AM. The SPRi measurements yield optical properties and thickness of the film by fitting the experimental data to the theoretical model of the SPRi system with four-layers –BK7 Prism, gold, Nafion, and air. The results show with increasing relative humidity to 93% the thickness of Nafion increases from 30 nm to 41±3 nm. The uncertainty in the thickness measurement is related to the angular resolution chosen for SRI with AM. This error could be minimized by running the visualization experiment with an angular resolution of less than 0.1 degree. The optical properties measurement indicates the refractive index of Nafion is decreased from 1.310 ± 0.002 at 3% RH to 1.228 ± 0.003 at 93% RH. Using Lorentz-Lorenz equation for a refractive index of a complex system, we found at smaller relative humidity level, 36% RH, the Nafion could confine water in the form of vapor in its structure. By increasing relative humidity to 93%, the Nafion could trap a mixture of water and water vapor in its void space. Our results show that SPRi can be used as an alternative visualization technique in studying confined thin PFSA ionomers.

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References

1. A. Kusoglu, *Fuel Cells and Hydrogen Production: A Volume in the Encyclopedia of Sustainability Science and Technology, Second Edition*, 417 (2019).
2. A. Kusoglu, A. Kwong, K. T. Clark, H. P. Gunterman and A. Z. Weber, *J. Electrochem. Soc*, **159**, F530 (2012).

3. A. Kusoglu and A. Z. Weber, *Chem. Rev.*, **117**, 987 (2017).
4. A. Kongkanand, *J. Phys. Chem.*, **115**, 11318 (2011).
5. D. J. Burnett, A. R. Garcia and F. Thielmann, *J. Power Sources*, **160**, 426 (2006).
6. A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner and A. Z. Weber, *Adv. Funct. Mater.*, **24**, 4763 (2014).
7. S. K. Dishari, C. A. Rumble, M. Maroncelli, J. A. Dura and M. A. Hickner, *J. Phys. Chem.*, **122**, 3471 (2018).
8. Y. Ogata, D. Kawaguchi, N. L. Yamada and K. Tanaka, *ACS Macro Lett.*, **2**, 856 (2013).
9. D. Paul, A. Fraser, J. Pearce and K. Karan, *ECS Trans.*, **41**, 1393 (2011).
10. S. A. Petrina, Water Sorption, Viscoelastic, and Optical Properties of Thin Nafion® Films, Pennsylvania State University, State College, PA (2013).
11. W. P. Kalisvaart, H. Fritzsche and W. Mérida, *Langmuir*, **31**, 5416 (2015).
12. W. Ogieglo, H. Wormeester, K.-J. Eichhorn, M. Wessling and N. E. Benes, *Prog. Polym. Sci.*, **42**, 42 (2015).
13. P. Nestler and C. A. Helm, *Opt. Express*, **25**, 27077 (2017).
14. J. N. Hilfiker, M. Stadermann, J. Sun, T. Tiwald, J. S. Hale, P. E. Miller and C. Aracne-Ruddle, *Appl. Surf. Sci.*, **421**, 508 (2017).
15. G. S. Hwang, D. Y. Parkinson, A. Kusoglu, A. A. MacDowell and A. Z. Weber, *ACS Macro Lett.*, **2**, 288 (2013).
16. S. Bayani, Y. Tabe, Y. T. Kang, S. H. Lee and C. K. Choi, *J. FLow Visualization and Image Process.*, **25** (2018).
17. C. H. Jeong, D. H. Shin, V. Konduru, J. S. Allen, C. K. Choi and S. H. Lee, *Int. J. Heat Mass Transf.*, **124**, 83 (2018).
18. M. Yamamoto, *Rev. Polarography*, **48**, 209 (2002).
19. D. Paul, Structure and Properties of Self-assembled Sub-micron Thin Nafion® Films, Queen’s University, Kingston, Ontario, Canada (2013).
20. W. Heller, *J. Phys. Chem.* , **69**, 1123 (1965).