3

Characterization of Nanocomposite Membranes

3.1 Introduction

Any membrane developed under a standard set of conditions, such as temperature and relative humidity needs to be characterized. Any small change in the conditions of membrane preparation may lead to a significant change in membrane structure and membrane morphology, which in turn may affect the membrane performance. The ultimate goal is to get membrane morphology to achieve desired performance. Membrane characterization is carried out to evaluate the structural membrane properties, such as pore size and pore size distribution, and the separation properties.

The methods of characterization for conventional membranes remain equally applicable for the nanocomposite membranes. The micrographic and spectroscopic methods become more important in terms of characterizing the nanomaterials embedded in the host matrix (polymer/ceramic).

The characterization methods can be classified into the following categories:

- Physical methods to determine pore size and pore size distribution
- Micrographic methods to have photographic images
- Spectroscopic methods to know the membrane structure in its molecular level
- Drop shape analysis (contact angle measurements) to ensure hydrophilicity/hydrophobicity of membrane surface
- Zeta potential measurement to ensure surface charge on membrane surface
- Methods to obtain bulk properties of membranes such as thermal and mechanical properties
3.2 Methods for Measurement of Pore Size and Pore Size Distribution

The following methods are used for the measurement of pore size and pore size distribution:

- Bubble gas transport method
- Mercury intrusion porosimetry
- Liquid–solid equilibrium method (thermoporometry)
- Gas–liquid equilibrium method (permporometry)
- Permeability method
- Solute rejection method

3.2.1 Bubble Gas Transport Method

The bubble gas transport method is based on the measurement of the pressure to blow air through a water-filled porous membrane. The method so developed has been used to characterize membranes and is called the bubble point method. The principle of the bubble point method is shown schematically in Figure 3.1. It can be seen from Figure 3.1 that the liquid on the top of the membrane wets the membrane surface. The bottom of the membrane is in contact with air and the air pressure is gradually increased until bubbles of air penetrate through the membrane.

An air bubble penetrates through a pore of radius \( r_p \) when the transmembrane pressure difference \( \Delta P = P_1 - P_2 \) given by the following Laplace equation is reached:

\[
\Delta P = 2\gamma / r_p
\]

FIGURE 3.1
Principle of the bubble point method.
Penetration will first occur through the largest pores, and because the pressure difference is known, the pore radius can be calculated from Equation 3.1. It is also possible to obtain pore size distribution by performing this technique by a stepwise increase of pressure. The method has been improved for both liquid–gas interfaces and liquid–liquid ones allowing the evaluation of pore sizes for a range of porous materials. This method is an easy, fast, and inexpensive method to determine the maximum pore size and pore size distribution of membranes. Though only active pores are measured, the disadvantage is that different results are obtained with different liquids. Liquid displacement is similar to gas bubble transport method, where a liquid is pressurized to displace the liquid in the pores. The disadvantage is that swelling is probable because of stagnant liquid in the pores, which can affect the pore size.

3.2.2 Mercury Intrusion Porosimetry

Mercury intrusion porosimetry is used extensively for the characterization of various aspects of porous media, including porous membranes and powders. It is applicable to pores ranging from 30 to 900°Å in diameter. It involves placing the sample in a special sample cup (penetrometer), surrounding the sample with mercury. Mercury is a nonwetting liquid to most materials and resists entering voids, doing so only when pressure is applied. The pressure at which mercury enters a pore is inversely proportional to the size of the opening to the void. As mercury is forced to enter pores within the sample material, it is depleted from a capillary stem reservoir connected to the sample cup. The incremental volume depleted after each pressure change is determined by measuring the change in capacitance of the stem. This intrusion volume is recorded with the corresponding pressure or pore size. By this technique, both pore size and pore size distribution can be determined. The relationship of pressure and pore size is given by the Laplace equation (3.1). As mercury does not wet the membrane (because its contact angle is greater than 90° and \( \cos \theta \) will have a negative value), Equation 3.1 is modified as follows:

\[
 r_p = -\left( \frac{2\gamma \cos \theta}{\Delta P} \right) \quad (3.2)
\]
The contact angle of mercury with polymeric material is often 141.3° and the surface tension at the Hg/air interface is 0.48 N/m. Hence, Equation 3.2 can be written as
\[ r_p = \frac{7492}{P} \] (3.3)

where:
- \( r_p \) is expressed in nanometer (nm)
- \( P \) is expressed in bar

The volume of mercury can be determined very accurately, which can result in the precise estimation of pore size distribution. In the above equation, it is assumed that the membranes have capillary pores. As in general, it is not always the case and morphology constant must be introduced. Also, very high pressure should be avoided as it may damage the porous structure and lead to an erroneous pore size distribution. Some of the disadvantages of this technique are as follows: (1) It needs high pressure that could damage the surface and (2) it measures all the pores present in the structure, including dead-end pores. The technique is not widely used due to the limitations.

### 3.2.3 Adsorption–Desorption Method

Gas adsorption is a popular and commonly used method for characterization of surface and structural properties of porous materials allowing the determination of their surface area, pore volume, pore size distribution, and adsorption energy distribution. Nitrogen is often used for the adsorbent gas, but other adsorbents such as argon and benzene are also used. According to this method, adsorption isotherm (the amount of adsorbed gas vs. the relative pressure) is drawn and the data are analyzed by assuming capillary condensation. The relative pressure is defined as the ratio of the adsorbent pressure to saturation vapor pressure of the adsorbent. The vapor pressure, \( p \), of the adsorbent liquid in the pore of radius \( r_p \) is given by the following Kelvin equation:

\[
\ln \left( \frac{p}{p_0} \right) = -\left( \frac{2\gamma V \cos \theta}{r_p RT} \right)
\] (3.4)

where:
- \( p_0 \) is the saturation vapor pressure
- \( \gamma \) is the surface tension of the adsorbent liquid
- \( V \) is the molar volume of the adsorbent liquid
- \( R \) is the universal gas constant
- \( T \) is the absolute temperature
- \( \theta \) is the contact angle
Assuming $\theta = 0^\circ$, the above equation becomes for the liquid nitrogen

$$r_p = -\frac{4.1}{\ln(p/p_0)} \quad (3.5)$$

Assuming further all the pores whose radii are smaller than $r_p$ are filled at a given relative pressure $p/p_0$, the cumulative pore volume curve versus $r_p$ can be drawn. Often, the thickness of adsorbed layer $t$ is added to $r_p$ to calculate more precise pore radius. Ceramic membranes often give better results because of their uniform structure and the membrane is less susceptible to capillary forces. Dead-end pores that do not contribute toward transport are also measured with this technique.

### 3.2.4 Liquid–Solid Equilibrium Method (Thermoporometry)

Thermoporometry is based on the calorimetric measurement of a solid–liquid transition in a porous material and can be applied to determine the pore size in porous membranes.\(^3\)–\(^5\) The temperature at which the liquid in the pore freezes depends on the pore size. As the pore size decreases, the freezing point decreases. Each pore gets its own specific freezing point. For cylindrical pores containing water,

$$r_p = 0.68 - \left(\frac{32.33}{\Delta T}\right) \quad (3.6)$$

where:
- $r_p$ is the pore radius
- $\Delta T$ is the extent of undercooling

As the pore radius decreases, the extent of undercooling increases. The heat effect of the liquid–solid transition is measured by means of a differential scanning calorimeter (DSC). All pores are measured with this technique including the dead-end ones.

### 3.2.5 Gas–Liquid Equilibrium Method (Permporometry)

Permporometry, unlike thermoporometry, characterizes only the active pores.\(^6\)–\(^7\) It is based on the blockage of the pores by means of a condensable gas, linked with the simultaneous measurement of gas flux through the membrane. This blockage is based on the same principle of capillary condensation as adsorption–desorption hysteresis. It is important that the vapor should be inert and should not swell the membrane; otherwise, the pore size will be affected. It is important to note that permporometry measures the active pores, whereas adsorption–desorption and thermoporometry
measure active, dead-end and even smaller pores in the sublayer. In case the membrane is asymmetric in nature, where the transport is governed by the thin top layer, this technique can give the information on pore size and pore size distribution of the top layer.

3.2.6 Permeability Method

Assuming the pores to be capillary in nature, the pore size can be determined by measuring the flux through a membrane at a constant pressure using Hagen–Poiseuille equation:

\[
J = \frac{\varepsilon r^2 \Delta P}{8 \eta \tau \Delta x}
\]

where:
- \(J\) is the flux through the membrane at a driving force of \(\Delta P/\Delta x\), with \(\Delta P\) being the pressure difference
- \(\Delta x\) is the membrane thickness

Other parameters are the pore radius \(r\), the liquid viscosity \(\eta\), the surface porosity of the membrane \(\varepsilon\), and the tortuosity factor \(\tau\). The pore size distribution can be obtained by varying the pressure, that is, by a combination of bubble point and permeability methods. It is not necessary that the liquid should wet the membrane.

The Hagen–Poiseuille equation assumes the pores to be cylindrical, which may not be the case. In that case, Kozeny–Carman equation can be used. It is assumed in this relation that the pores are interstices between close-packed spheres. The flux is given by

\[
J = \frac{\varepsilon^3 \Delta P}{K \eta S^2 (1-\varepsilon)^2 \Delta x}
\]

where:
- \(K\) is the membrane constant, called the Kozeny–Carman constant, which is dependent on the pore shape and tortuosity
- \(\varepsilon\) is the porosity
- \(S\) is the specific surface area

The permeability method is widely used for both microfiltration and ultrafiltration membranes. This method is entirely based upon the assumptions taken toward the pore geometry which is largely unknown, and hence, the experimental results are difficult to interpret.
3.2.7 Solute Rejection Method

This is the method frequently used for industrial assessment of membranes. Usually, membrane manufacturers use the concept of cutoff to characterize the ultrafiltration membranes. Cutoff is defined as the molecular weight that is 90% rejected by the membrane. The membrane has a cutoff value of 40,000, which implies that all solutes with a molecular weight greater than 40,000 are rejected by the membrane by more than 90%. However, it is not possible to define the separation characteristics of a membrane by this single parameter, that is, molecular weight of solute, because the parameters such as shape, flexibility of macromolecular solute, and its interaction with the membrane material are all important to be taken into account. However, concentration polarization and membrane fouling can affect the separation performance of the membrane. Cutoff values are often expressed in different ways under different test conditions (pressure, geometry of test cell, type and concentration of solute, cross-flow velocity, and more importantly molecular-weight distribution of solute), which makes it difficult to hold a comparison of the results obtained.

3.3 Micrographic Methods

Micrographic methods are more pronounced where the structure of nanocomposites usually consists of the matrix material containing the nanosized reinforcement components in the form of particles, whiskers, fibers, nanotubes, and so on. These characterization techniques help to understand the correlation between structure and performance of a particular nanocomposite membrane.

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Atomic force microscopy (AFM)

3.3.1 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons. The electrons interact with the atoms that make up the sample-producing signals that contain information about the sample’s surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by a SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), and specimen current and transmitted electrons. Secondary electron
detectors are common in all SEMs. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging, the SEM can produce very high-resolution images of a sample surface, revealing details of about 5–20 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional (3D) appearance useful for understanding the surface structure of a sample. A wide range of magnification is possible, from about 10 times (about equivalent to that of a powerful hand lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. BSEs are beam electrons that are reflected from the sample by elastic scattering. They are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number \((Z)\) of the specimen, BSE images can provide information about the distribution of different elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. Other types of electron emitters include lanthanum hexaboride \((\text{LaB}_6)\) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded, and field emission guns, which may be of the cold cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide.

The electron beam, which typically has an energy ranging from 0.5 to 40 keV, is focused by one or two condenser lenses to a spot about 0.4–5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the \(x\) and \(y\) axes so that it scans in a raster fashion over a rectangular area of the sample surface. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image can be captured from a high-resolution cathode ray tube. It can be digitally captured and displayed on a computer monitor and saved to a computer’s hard disk. Depending on the instrument, the resolution can fall somewhere between less than 1 and 20 nm. SEM gives information about topography, that is, surface features, and its textures as well as morphology, that is, shape and size of the particles. It also furnishes information about the elements and compounds that the object is composed of. In other words, SEM furnishes direct relationship between features and material properties, structure and material properties as well as composition and material properties.

The method that is suitable for the direct estimation of surface porosity is electron microscopy. A major drawback of electron microscopy is that microscopic analysis is very local and that the resolution is insufficient to study...
Characterization of Nanocomposite Membranes

fine porous structures. Also, the method becomes very laborious when a reasonable level of precision has to be reached because it is necessary to count and measure a large number of pores. The processing of the data is time consuming, although computer-aided image analysis can be used. Top layer thickness is one of the parameters frequently estimated from electron microscopic pictures. Asymmetry in composite membranes can also be readily observed. SEM has been used to study polysulfone/sulfonated polyether ether ketone (SPEEK) membranes. Changes in pore structure resulting from different casting conditions and composition are shown in Figure 3.2. Obtaining cross-sectional samples usually involves razor blades and can result in compression and tearing. The direct freeze fracture method, where a membrane is made brittle in liquid nitrogen and is then broken, can be used. The preparation of a thin film, as is required in transmission electron microscope (TEM), is not required for SEM. The disadvantage is that the membrane pore structure can be affected by drying and coating, so SEM-observed porosity may not exactly correspond to in situ membrane porosity.

3.3.2 Transmission Electron Microscopy

In TEM, an image is produced by passing electrons under high vacuum through a sample. The electron beam typically has an energy ranging from 100 to 300 keV. The image is formed from the interaction of the electrons transmitted through the specimen, which is magnified and focused onto an imaging device, such as a fluorescent screen, or on a layer of photographic film, or to be detected by a sensor. Near-atomic resolution is attainable using TEM; however, this technique is limited to thin samples which are at most several tens of nanometers in thickness. Therefore, TEM is restricted to imaging thin-film samples rather than fully constructed membranes. As an example, a TEM image of a graft copolymer is shown in Figure 3.3. It may be concluded that the differences in electron densities between the two components of this amphiphilic graft copolymer were sufficient to be observed as image contrast. Dark regions represent the hydrophobic crystalline regions of the main chains, whereas lighter regions represent the hydrophilic side chains.

In terms of sample preparation, the vacuum environment requires dry samples. Also, coating may be necessary to prevent sample destruction by the electron beam.

3.3.3 Atomic Force Microscopy

Surface roughness of the membranes can be measured with atomic-level resolution using AFM. AFM is a nonoptical surface imaging technique that approaches atomic resolution. The atomic force microscope (AFM) consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip
radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, and solvation forces. Along with force, additional parameters may simultaneously be measured through the use of specialized types of probe.

**FIGURE 3.2**
Scanning electron microscope images (200x) of cross sections of polymer blend membranes. (Reprinted from *J. Membr. Sci.*, 324, Li, X., De Feyter, S., and Vankelecom, I.F.J., Poly(sulfone)/sulfonated poly(ether ether ketone) blend membranes: Morphology study and application in the filtration of alcohol based feeds, 67–75, Copyright 2008, Figure 1, with permission from Elsevier.)
Characterization of Nanocomposite Membranes

(scanning thermal microscopy, scanning Joule expansion microscopy, photothermal microspectroscopy, etc.). The deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing, or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases, a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively, a tripod configuration of three piezo crystals may be employed, with each responsible for scanning in the x, y, and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner, whereas the sample is being scanned in X and Y using another piezo block. The resulting map of the area \( z = f(x, y) \) represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or noncontact) modes where the cantilever is vibrated. The membrane surface can be scanned in vacuum, air,
or water, and no sample preparation is necessary. An example illustration of an AFM experimental setup is given in Figure 3.4. Based on the sample profile, \( h(x, y) \), it is possible to calculate mean and root mean square (RMS) roughness (\( R_a \) and \( R_{rms} \), respectively) and 10-point mean roughness (\( R_z \)) parameters. There is a relationship between \( R_a \) and the water flux and separation performance of hollow-fiber UF membranes.\(^{13}\) As \( R_a \) decreases, flux decreases and rejection increases.

### 3.4 Spectroscopic Methods

Under this category, the following techniques are widely used:

- Infrared (IR) and Fourier transform IR (FTIR) spectroscopy
- X-ray photoelectron spectroscopy (XPS)
- Energy-dispersive X-ray spectroscopy (EDS or EDX)
- Positronium annihilation lifetime spectroscopy (PALS)

#### 3.4.1 Attenuated Total Reflection FTIR Spectroscopy

The principle of attenuated total reflection FTIR (ATR-FTIR) is based on the total internal reflection phenomenon. A block of material with greater optical density than the sample is put into close contact with the sample surface.
The incident radiation angle must be greater than the critical angle value. The evanescent field decays exponentially into the sample. The principle of ATR-FTIR is shown in Figure 3.5. ATR-FTIR spectroscopy allows for IR analysis of surfaces. The IR spectrum can provide determination of vibrational frequencies and transition intensities of most molecules (with the exception of diatomics such as N\(_2\) and O\(_2\)), including characteristic functional group frequencies. Knowledge of vibrational frequencies of functional groups (or reference spectra) allows for chemical identification of at least a class of compounds (e.g., aromatic amides). IR radiation typically penetrates 1 \(\mu\)m into the surface, which is a disadvantage because this is deeper than the active layer thickness of most composite membranes, so the top layer is not necessarily isolated. The penetration depth can be decreased by careful selection of crystal and incident angle. Alternatively, it is possible to perform ATR-FTIR measurements of both sides of an asymmetric membrane and then to essentially subtract out the support layer spectral regions.

Vibrational frequencies cannot be easily converted into complete chemical structure of the material, but can provide more molecular structure information than XPS.

### 3.4.2 X-Ray Photoelectron Spectroscopy

In XPS, the sample surface is subjected to X-ray radiation capable of removing electrons from the inner shells of the atoms (except H and He). The amount of emitted electrons is recorded as a function of binding energy. Surface depths of 0.5–10 \(\text{nm}\) can be probed, depending on the incident beam angle. The inner shell energies are characteristic for a given element, but sensitive to the external chemical environment. For carbon, this chemical shift can amount to a few electronvolts. For the carbonyl group (C=O), the binding
energy is 285 eV, and for the methylene group (CH\textsubscript{2}), the binding energy is 287.8 eV. Routine detection limits are 0.1\%. From the emitted electron intensities, surface atomic concentrations can be found out through empirical formulae. XPS results for a variety of membranes are reported in Table 3.1.\textsuperscript{15} The advantage of XPS is the requirement of shallow probing depth (i.e., it obtains information about the near membrane surface rather than the membrane interior). It has the ability to characterize the elemental composition of the membrane surface. However, chemical identity of the polymer (or additives) cannot be deduced based on elemental composition alone.

### 3.4.3 Energy-Dispersive X-Ray

EDS or EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. It is based on the principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element’s atomic structure to be identified uniquely from one another.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample. At rest, an atom within the sample contains ground-state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole. An electron from an outer, higher energy shell then fills the hole, and the difference in energy between the higher energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between

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<th>TABLE 3.1</th>
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<tr>
<td>Measured Atomic Concentration Percentages (%) of C\textsubscript{1s}, O\textsubscript{1s}, N\textsubscript{1s}, and S\textsubscript{2p} Obtained by XPS for Commercially Available and Experimental Membranes</td>
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<tr>
<td>NF270</td>
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<tr>
<td>C\textsubscript{1s}</td>
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the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. There are four primary components of the EDX setup: the beam source, the X-ray detector, the pulse processor, and the analyzer. A number of free-standing EDX systems exist. However, EDX systems are most commonly found on scanning electron microscopes (SEM-EDX) and electron microprobes. SEMs are equipped with a cathode and magnetic lenses to create and focus a beam of electrons, and since the 1960s, they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. Typical EDX analyses of polysulfone and silver–polysulfone nanocomposite membrane are shown in Figure 3.6a and b, respectively.\(^\text{16}\)

**FIGURE 3.6**
(a) EDX spectra of polysulfone membrane surface. (b) EDX spectra of polysulfone–silver membrane surface. (Data from Kar, S. et al., *Desalination Water Treat.*, 27, 224–230, Copyright 2011, Figures 5 and 6, Taylor & Francis Group.)
3.4.4 Positronium Annihilation Lifetime Spectroscopy

PALS measures positronium (Ps) annihilation lifetimes and intensities, which can be related to the size and amount of defect structures, such as voids or pores in the range of several angstroms to tens of nanometers. It has tremendous potential\cite{17-19} as a powerful tool for quantifying the types and densities of defects in solids. Following the injection of positrons into a solid material, the positrons pair-annihilate at a rate depending on the density of electrons near the injection site. If there are lattice vacancy or dislocation defects (voids) near the injection site, the positrons are attracted to these areas, which have lower electron densities and thus give rise to longer positron lifetimes. This is suitable for insulating materials while not good in the bulk of metals because Ps cannot be formed in the latter. A beam of monoenergetic low-energy positrons (several kiloelectronvolts) is used for thin-film study. Thickness of the film can vary from several nanometers to a few microns. The energy of the implanted positrons is tunable, which enables PALS to depth profile thin films. By comparison, positrons typically used for bulk PALS have an implantation depth of 0.2–0.3 mm and as such are unsuitable for probing thin films.

PALS is a unique and valuable technique that characterizes the free-volume hole properties in solid polymeric systems\cite{20,21} based on the detection of $\gamma$-radiation.\cite{22} When positrons from a $^{22}$Na radioisotope source are injected into a polymer, they lose their kinetic energy. After thermalization occurs in the sample, the positrons either (1) diffuse into the media and become annihilated as a free positron with an electron in about 0.4 ns (free positron annihilation) or (2) capture an electron from the material and form a bound-state Ps of two spin states, that is, $\text{para-Ps}$ ($p$-Ps) or $\text{ortho-Ps}$ ($o$-Ps). In polymers, the $o$-Ps lifetime is shortened to a few nanoseconds through the trapping in molecular free volumes and the annihilation with an electron from the inner wall of the free volume (annihilation of $o$-Ps). The lifetime of $o$-Ps has been proven to be highly correlated with the average size and distribution of hole spaces present in the solid polymers; the longer the lifetime of $o$-Ps, the larger the $R$, and vice versa.\cite{23,24} The spectral intensity associated with this lifetime component is related to the number of free volume hole sites if no Ps-quenching functional groups exist in the molecular structure of polymers, which is expected to provide a better understanding of the flux enhancement and eventually could aid in design of new TFC membranes that display outstanding performance.

3.4.5 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the
Characterization of Nanocomposite Membranes

105

Characterization of Nanocomposite Membranes

sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational, and other low-frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid, and gaseous samples. This is a complementary method to IR spectroscopy. It is an alternative technique for molecular identification. In particular, Raman spectroscopy provides information about functional groups (\(-\text{C}--\text{S}--\), \(-\text{C}--\text{C}--\), \(-\text{C}--\text{H}--\) etc.), which are important in membrane technology. Raman spectroscopy has been used to examine changes in polymer structure in the membrane and to characterize membrane morphology. Raman techniques require no special sample preparation and produce cleaner, narrower spectra than IR, making band interpretation more robust. However, because of the inherently weak signals and interference from fluorescence, the technique has not gained significant attention for identification of organic compounds. Surface-enhanced Raman spectroscopy is an extension of Raman spectroscopy that allows both an enhanced Raman signal and substantial quenching of fluorescence through the use of coinage metal nanostructures (silver, gold, etc.), thus offering highly specific molecular-level identification of extremely small samples and samples capable of fluorescence.\(^25,26\) It allows nondestructive characterization of organics. Nafion membranes have been studied earlier by IR and Raman spectroscopy.\(^27,28\)

3.4.6 Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) is a neutron scattering technique that enables the study of materials on the nanometer to micrometer length scales. The experiment consists of a well-collimated beam of neutrons being passed through a sample and detectors to count the number of neutrons scattered as a function of angle and neutron wavelength. This data is used to extract information about the shape, size, arrangement, and interactions of the components of the sample.

SANS technique finds particular use in the study of soft matter (e.g., colloids and polymers), biophysics (e.g., lipids and lipid–protein complexes), biology (e.g., solution structures of proteins), and hard condensed matter (e.g., superconductors and magnetic materials). SANS has been used to characterize a phospholipid/alkoxysilane hybrid bilayer membrane at the interface of porous aluminum oxide films.\(^29\)

3.4.7 Small-Angle X-Ray Scattering

The small-angle X-ray scattering (SAXS) technique is based on the detection of the elastic scattering of X-rays by samples with inhomogeneities of the electron density in the nanometer range. X-ray scattering in the small-angle range contains information about the shape and size of nano-objects in
dilute solution such as macromolecules, characteristic distances of partially ordered nanostructured materials, nanopore sizes, and other low-resolution structure features. SAXS provides structural parameters of macromolecules with sizes between 5 and 25 nm.

In small-angle scattering technique, a sample is irradiated with a well-collimated beam of radiation such as X-rays, neutrons, or light; the resulting intensity is measured as a function of angle between the incoming beam and the scattered beam; and then the structure that caused the observed pattern is determined. Scattering patterns are caused by the interference of secondary waves that are emitted from various structures when irradiated, that is, electrons for X-rays and light, or nuclei for neutrons. Scattering of X-rays is caused by differences in electron density. Scattering of neutrons is caused by differences in scattering power of different nuclei. Scattering of light is caused by differences in refractive index. The larger the diffraction angle, the smaller the length scale probed; wide-angle X-ray scattering is used to determine crystal structure on the atomic length scale, whereas SAXS or SANS is used to explore the microstructure on the colloidal length scale. Unlike an electron micrograph, SAXS patterns do not give morphological information directly. The result of a SAXS experiment is essentially the intensity of the Fourier transform of the electron density and must be interpreted in order to determine morphology. One fundamental problem with any scattering experiment is that two different morphologies can, in theory, give identical scattering patterns. Generally, one cannot reconstruct the exact microstructure uniquely from a SAXS pattern because in a scattering experiment only the scattered radiation intensity can be measured and all phase information is lost. Therefore, one cannot be absolutely sure that a scattering pattern is due to a particular morphology. Nanopores are characterized in track-etched polymer membranes using SAXS. Improved performance of phosphonated carbon nanotube–polybenzimidazole composite membranes in proton-exchange membrane fuel cells is supported by the SAXS studies.

3.4.8 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is a powerful and theoretically complex analytical tool. It is based on the fact that when a population of magnetic nuclei is placed in an external magnetic field, the nuclei become aligned in a predictable and finite number of orientations. For $^1$H there are two orientations: In one orientation, the protons are aligned with the external magnetic field (north pole of the nucleus aligned with the south pole of the magnet and south pole of the nucleus with the north pole of the magnet) and in the other orientation, the nuclei are aligned against the field (north with north and south with south). The alignment with the field is also called the alpha orientation and the alignment against the field is called the beta orientation. The NMR spectroscopy experiment involves using energy in the form of electromagnetic radiation to pump the excess alpha-oriented
nuclei into the beta state. When the energy is removed, the energized nuclei relax back to the alpha state. The fluctuation of the magnetic field associated with this relaxation process is called resonance, and this resonance can be detected and converted into the peaks, which is seen in an NMR spectrum. Membrane proteins are important targets for structure determination. Protein structure determination\(^{32,33}\) has played a key role in biomedical research for more than 60 years. NMR spectroscopy is particularly well suited for determining the 3D structures of proteins and for describing their local and global motions in lipid environments, where they maintain their native conformation.

### 3.4.9 Electron Spin Resonance

Electron spin resonance (ESR) is also known as the electron paramagnetic resonance (EPR). Paramagnetic molecules have unpaired electrons, and while changing the magnetic field, these will absorb energy at particular values of the field. This absorption is due to a change in direction of the magnetic moment resulting from the electron’s spin. The absorption spectra that are produced can give information about the structure of free radicals and complex ions. ESR works on the same principle as NMR, except that microwave (rather than radiowave) frequencies are employed and spin transitions of unpaired electrons rather than nuclei are recorded. Unlike NMR spectra, where absorption is recorded directly, ESR spectrometers plot the first derivative of the absorption curve. ESR permits observation of any substance having unpaired electrons. It is sensitive to local environment. Polymers themselves contain paramagnetic free radicals. The free radicals do take part in the transportation of gases through the membrane.$^{34,35}$

### 3.5 Contact Angle Goniometer

Contact angle goniometer is used to measure the static contact angle, advancing and receding contact angles, and surface tension. The first contact angle goniometer was designed by William Zisman. The original manual contact angle goniometer used an eyepiece with microscope. The current generations of contact angle instruments use cameras and software to capture and analyze the drop shape suitable for dynamic and advanced studies. A gonioreflectometer is used to measure the reflectivity of a surface at a variety of angles.

The contact angle, \( \theta \), is the angle formed by a liquid at the three-phase boundary where the liquid, gas, and solid intersect. The contact angle depends on the interfacial tensions between the gas and liquid, liquid and solid, and gas and solid. Young’s relation expresses the contact angle analytically.
\[ \gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta \]  

where:

- \( \gamma_{SG} \) is the interfacial tension between the solid and the gas
- \( \gamma_{SL} \) is the interfacial tension between the solid and the liquid
- \( \gamma_{LG} \) is the interfacial tension between the liquid and the gas

Contact angle goniometer measures a droplet’s contact angle by assuming that the droplet fits the geometry of a sphere, an ellipsoid, or the Young–Laplace equation.

Contact angle is the ratio of cohesion force to adhesion force. Cohesion is the force between the liquid molecules that hold the liquid together. Adhesion is the force between the liquid molecules and the solid molecules. If the contact angle is near zero, meaning that the liquid droplet spreads completely on the solid surface, adhesive forces are dominating. If the contact angle is very high, meaning that the liquid droplet beads up on the solid surface as water does on a freshly waxed car, cohesive forces are dominating.

Although static contact angle gives static information about the interfacial tensions between the solid, the liquid, and the gas; advancing and receding contact angles give some information about the dynamic interaction of the liquid, solid, and gas. An advancing contact angle is determined by pushing a droplet out of a pipette onto a solid. When the liquid initially comes into contact with the solid, it forms some contact angle. As the pipette injects more liquid through the pipette, the droplet increases in volume and the contact angle increases, but its three-phase boundary remains stationary until it suddenly jumps outward. The contact angle the droplet has immediately before jumping outward is termed the advancing contact angle. The droplet will decrease in volume and the contact angle decreases, but its three-phase boundary remains stationary until it suddenly jumps inward. The contact angle the droplet has immediately before jumping inward is termed the receding contact angle. The receding contact angle is measured by sucking the liquid back out of the droplet. The difference between advancing and receding contact angles is termed as contact angle hysteresis, which can be used to characterize surface heterogeneity, roughness, and mobility.

The contact angle (\( \theta \)) that is formed at the three-phase interface between solid, liquid, and gas/vapor phases is used to elicit information regarding membrane surface energy properties. The information that is gathered from contact angle analysis may be used to calculate specific surface energy properties (van der Waals, Lewis acid–base) for a detailed interfacial analysis, as well as for qualitatively assessment of the wettability, or hydrophobicity/hydrophilicity, of membrane surface. The greatest challenge with goniometric contact angle measurements is contact angle hysteresis, which is the difference in the measured contact angle depending on whether it is an advancing or receding measurement. The important issue for contact
Characterization of Nanocomposite Membranes

Angle measurement reproducibility is the effect of drop and bubble size on the contact angle. The advancing angle should be more reproducible, as it depends on the bubble/drop size to a lesser degree, on both smooth and imperfect surfaces.\textsuperscript{36,37} However, information on surface quality that can be gained from receding angle/bubble size relationship will be lost if only advancing angle is measured. Multiple linear regression has been used to study the influence of surface hydrophobicity, surface roughness, surface charge, molecular-weight cutoff, permeability, and porosity of the top layer on nanofiltration membrane performance.\textsuperscript{38} Contact angle, volume fraction of small pores, and membrane charge are the significant variables in predicting relative flux. Contact angle measurements are useful in membrane integrity testing.

3.6 Zeta Potential Measurements

Zeta potential (\(\zeta\)) is the potential difference between the bulk of solution and the sheer (slipping) plane of the interfacial double layer. It is a function of surface and solution chemistry (pH, ionic composition, and ionic strength) at the solid–liquid interface and is an important membrane characteristic for assessing membrane fouling potential and developing chemical cleaning protocols. Membrane zeta potential is typically determined from streaming potential measurements. A streaming potential is generated when an electrolyte solution flows through a thin channel or porous media (e.g., a sand column) and is related to zeta potential by the Helmholtz–Smoluchowski equation:

\[
\frac{E}{P} = \frac{\varepsilon \varepsilon_0 \zeta}{\lambda \eta}
\]  

(3.10)

where:

- \(E\) is the streaming potential due to electrolyte flow through a capillary channel
- \(P\) is the applied pressure driving the flow
- \(\zeta\) is the zeta potential
- \(\lambda\) is the electrolyte conductivity
- \(\eta\) is the viscosity of the electrolyte solution
- \(\varepsilon\) is the relative permittivity of the solution (dimensionless)
- \(\varepsilon_0\) is the vacuum permittivity (fundamental constant)

The values of \(E\), \(P\), and \(\lambda\) are measured by the streaming potential analyzer, whereas \(\varepsilon\) and \(\eta\) are calculated based on temperature measurement.
In experimental investigations of membrane charge, streaming potential measurements are used to calculate zeta potential. Streaming potential is the potential induced when an electrolyte solution is pumped across a stationary charged surface. It can be used to calculate zeta potential using the Helmholtz–Smoluchowski equation, which relates the pressure dependence of streaming potential to the properties of the solution, that is, conductivity and viscosity. Unlike earlier streaming potential investigations, now the streaming potential is measured over a range of solution pH. Surface charge as a function of pH is crucial for understanding the acid–base properties of membrane surface functional groups.

Although streaming potential measurements are the most frequently used method for evaluating charge properties, there are concerns with respect to the effect of membrane roughness on the measurement, the relationship between the measured zeta potential and the double layer structure, the inherent assumptions of the Helmholtz–Smoluchowski equation (i.e., laminar flow), and the lack of a calibration standard. However, zeta potential from streaming potential measurement is one of the few techniques capable of describing the charge properties of membranes.

### 3.7 Differential Scanning Calorimetry

The DSC is used for thermal analysis of nanomaterials and polymers. The information is used to understand amorphous and crystalline behavior, polymorph and eutectic transitions, curing and degree of cure, and many other material properties used to design, manufacture, and test products. A sample of known mass is heated or cooled and the change in its heat capacity is monitored. The DSC measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes. It is used to determine the melting behavior of complex organic materials; both temperatures and enthalpies of melting can be used to determine purity of a material. It is also widely used to measure material glass transition temperatures or softening temperatures of plastic or glassy materials, which change depending upon the temperature history of the polymer or the amount and type of fill material, among other effects. It can determine the crystalline-to-amorphous transition temperatures in polymers and the energy associated with the transition. The biggest advantage of DSC is the ease and speed with which it can be used to see transitions in materials. A schematic DSC curve for a semicrystalline polymer is shown in Figure 3.7 illustrating the possible heat effects. Such DSC curves allow the glass transition temperature and the degree of crystallinity to be obtained. Both first-order and second-order transitions are observed in Figure 3.7.
The former transitions, referred to as crystallization and melting, give narrow peaks (the peak area being proportional to the amount of crystalline material present). The glass transition temperature corresponds to second-order transition. Studies have been carried out to see the effects of nanoparticles on the glass transition temperature of the prepared nanocomposite membranes by DSC, where the glass transition temperature of nanocomposite membranes was found to increase with nanoparticle incorporation.42–44

### 3.8 Tensile Strength Measurements

Tensile strength measurements are done by universal testing machine. By pulling the material, it is determined that how the material will react to forces being applied in tension. By continuing to pull on the material until it breaks, a good, complete tensile profile of the material can be obtained. A curve will result, showing how it reacted to the forces being applied. The point of failure is of much interest and is typically called its ultimate strength.

For most tensile testing of materials, in the initial part of the test, when a material deforms elastically, the amount of deformation depends on the size of the material, but the strain for a given stress is always the same and the two are related by Hooke’s law (stress is directly proportional to strain):

$$ E = \left( \frac{\sigma}{\varepsilon} \right) $$

(3.11)

where:

- $\sigma$ is the stress
- $E$ is the modulus of elasticity
- $\varepsilon$ is the strain
$E$ is the slope of the line in this region where stress ($\sigma$) is proportional to strain ($\varepsilon$) and is called the *modulus of elasticity* or *Young’s modulus*. The modulus of elasticity is a measure of the stiffness of the material. If a specimen is loaded within this linear region, the material will return to its exact same condition if the load is removed. At the point that the curve is no longer linear and deviates from the straight-line relationship, Hooke’s law no longer applies and some permanent deformation occurs in the specimen. This point is called the *elastic or proportional limit*.

From this point on in the tensile test, the material reacts plastically to any further increase in load or stress. It does not return to its original, unstressed condition if the load is removed. A parameter called *yield strength* of a material is defined as the stress applied to the material at which plastic deformation starts to occur although the material is loaded. The amount of stretch or elongation the specimen undergoes during tensile testing can also be found out. This can be expressed as an absolute measurement in the change in length or as a relative measurement called *strain*. Strain can be expressed as the ratio of the change in length to the original length:

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l_1 - l_0}{l_0}$$  \hspace{1cm} (3.12)

where:

- $\Delta l$ is the change of the length
- $l_1$ is the length after elongation
- $l_0$ is the original (initial) length

The *ultimate tensile strength* of a material is the maximum load the specimen sustains during the test. It may or may not equate to the strength at break. This depends on the type of material under testing.

As membranes vary in chemical and material composition, test methods are prescribed in various standards, which specify different specimen shapes, sizes, grip lengths, and loading speeds. Some of these *standard test methods*, frequently referred to in testing of roofing membranes or similar materials, are presented in Table 3.2.  

It is seen that the temperature, speed of loading, gauge length, and strain variation within a specimen affect the tensile tests of a membrane sample.

Nanoparticles have great potential in improving the mechanical properties of the membrane. In particular, PVDF flat sheet membrane with 0.54 wt.% of SBA-15 (a mesoporous silica material with a highly ordered two-dimensional hexagonal mesostructure and thick uniform silica walls) increases tensile strength from 0.151 to 0.183 MPa, whereas that loaded with 0.36 wt.% increased elongation at break from 22.6% to 49.4%. Likewise, PVDF nanocomposite membranes incorporated with ZnO nanoparticles exhibits increased tensile strength and elongation at break.

PVDF/TiO$_2$ hollow-fiber membranes
### TABLE 3.2

**ASTM Standards Applicable to Properties of Roofing Membrane Material Where Tensile Testing Is Involved**

<table>
<thead>
<tr>
<th>ASTM Standard</th>
<th>ASTM Designation</th>
<th>Shape</th>
<th>Specimen Width (mm)</th>
<th>Gauge or Grip Length (mm)</th>
<th>Rate of Grip Separation (mm/min)</th>
<th>Approximate Operating Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D146</td>
<td>Bitumen-saturated felts and woven fabrics for roofing and waterproofing</td>
<td>Rectangular</td>
<td>25</td>
<td>100</td>
<td>51</td>
<td>15</td>
</tr>
<tr>
<td>D412</td>
<td>Rubber properties in tension</td>
<td>Dumbbell</td>
<td>6</td>
<td>33</td>
<td>510</td>
<td>30</td>
</tr>
<tr>
<td>D624</td>
<td>Rubber property—tear resistance</td>
<td>Curly and notched</td>
<td>19</td>
<td>58</td>
<td>450–550</td>
<td>25</td>
</tr>
<tr>
<td>D638</td>
<td>Tensile properties of plastic</td>
<td>Dumbbell</td>
<td>6</td>
<td>25</td>
<td>50–500</td>
<td>30–300</td>
</tr>
<tr>
<td>D751</td>
<td>Coated fabrics</td>
<td>Rectangular (grab)</td>
<td>100</td>
<td>75</td>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>D882</td>
<td>Tensile properties of thin plastic sheeting</td>
<td>Rectangular</td>
<td>5–25</td>
<td>50–125</td>
<td>12.5–500</td>
<td>15–120</td>
</tr>
<tr>
<td>D1004</td>
<td>Initial tear resistance of plastic film and sheeting</td>
<td>Curly and notched</td>
<td>19</td>
<td>25</td>
<td>51</td>
<td>20</td>
</tr>
<tr>
<td>D2523</td>
<td>Load–strain properties of roofing membranes</td>
<td>Dumbbell</td>
<td>25</td>
<td>76</td>
<td>1.3–500</td>
<td>3–1500</td>
</tr>
<tr>
<td>D2707</td>
<td>Hard rubber in tension</td>
<td>Dumbbell</td>
<td>12.5</td>
<td>75</td>
<td>5–10</td>
<td>90</td>
</tr>
<tr>
<td>D4073</td>
<td>Tensile tear strength of bituminous roofing membranes</td>
<td>Rectangular and notched</td>
<td>75</td>
<td>100</td>
<td>2.5</td>
<td>30</td>
</tr>
</tbody>
</table>

*Note: ASTM, American Society for Testing and Materials.*
Nanocomposite Membrane Technology

prepared by either TiO$_2$ sol–gel or blending method shows 30% increase in tensile strength.\textsuperscript{48} However, elongation at break decreases from 162% to 120% likely due to the rigidity of the inorganic particles. The improvement in tensile strength is attributed to the reduced macro-void formation observed in the nanocomposite membranes. The decreased ductility could be owing to the increased cross-linking arising from the nanoparticle inclusion rather than the brittleness of the particles.

3.9 Methods to Characterize Proton-Exchange Membranes

In addition to the above-mentioned different characterization techniques, specific methods are adopted for characterization and testing of proton-exchange membranes.

3.9.1 Water Uptake Measurement

In case of proton-exchange membranes, the ion-exchange capacity is linked with the water uptake capacity of the membrane, due to migration methods presented in proton-exchange membranes, which are mainly Grothuss and vehicular mechanisms. In the Grothuss mechanism, protons jump from an H$^+$ donor site to any receiving water molecule in the vicinity, forming an H$_3$O$^+$ complex, whereas in the vehicular mechanism, protons are transferred through hydronium ions. The presence of water is necessary for proton conduction in both mechanisms.\textsuperscript{49} For the water uptake measurement, a sample of the dry membrane prepared is weighed\textsuperscript{50} and immersed in distilled water for 24 h, then excess water is removed with absorbent paper and the wet sample is weighed. The water uptake is calculated according to the following equation:

$$\% \text{ water uptake} = \frac{w_w - w_d}{w_d} \times 100 \quad (3.13)$$

where:
\begin{itemize}
  \item $w_w$ is the weight of wet sample
  \item $w_d$ is the weight of dry sample
\end{itemize}

3.9.2 Ion-Exchange Capacity Measurement

The ion-exchange capacity is measured by a classic titration method. Initially, the membranes is converted to its proton form by soaking them in 1 M HCl solution for 24 h.\textsuperscript{51} Subsequently, the membranes are washed with distilled water and immersed in a 1 M solution of NaCl for 24 h, to perform the exchange of H$^+$ protons for Na$^+$ ions. Then the solution with H$^+$ protons is
Characterization of Nanocomposite Membranes

titrated with a 0.01 M NaOH solution using phenolphthalein indicator. The ion-exchange capacity was calculated according to the following equation:

$$\text{IEC (meq/g dry sample)} = \frac{V M}{W}$$  \hspace{1cm} (3.14)

where:

- IEC is the ion-exchange capacity
- $V$ is the volume of the titrant solution when equilibrium point is reached
- $M$ is the concentration of titrant solution
- $W$ is the weight of the dry sample

3.9.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful diagnostic tool that can be used to improve the performance of the fuel cells. It is frequently used for the determination of proton and ionic conductivity of proton-exchange membranes. There are three fundamental sources of voltage loss in fuel cells: (1) charge transfer activation or kinetic losses, (2) ion and electron transport or ohmic losses, and (3) concentration or mass transfer losses. The EIS technique is used to measure the frequency dependence of the impedance of a fuel cell by applying a small sinusoidal AC potential (or current) as a perturbation signal to the fuel cell and measuring the current (or potential) response. The application of EIS in proton-exchange membrane fuel cell studies involve the following: (1) to provide microscopic information about the fuel cell system, which can help in fuel cell structure optimization and the selection of the most appropriate operating conditions; (2) to allow modeling of the system with an appropriate equivalent circuit and consequently to obtain the electrochemical parameters of the system; (3) to differentiate the individual contributions of each component, such as the membrane and the gas diffusion electrode, to fuel cell performance, which can assist in identifying problems within the fuel cell components; and (4) to identify individual contributions to the total impedance of a PEM fuel cell from different electrode processes such as interfacial charge transfer and mass transport in both the catalyst layer and the backing diffusion layer.52–54

References


