CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1. FT-IR

The chemical structures of the anion-exchange materials and anion-exchange membranes were characterized by Fourier transform infrared spectroscopy (FT-IR) using Perkin Elmer spectrum Two instrument (Model L160000A) in the range of 4000-400 cm\(^{-1}\). The measurements were performed using an attenuated total reflectance (ATR) attachment. Dry and clean samples were pressed onto the crystal, without any further sample preparation.

2.2. X-ray powder diffraction

The synthesized powders were characterized by X-ray powder diffraction (XRD). XRD patterns were recorded with a SHIMADZU, XRD 700 powder diffractometer operated at 35 kV voltage and 30 mA current using CoK\(\alpha\) radiation. Data were scanned in the angular range 20-80° (2θ), with a step size of 0.0196°/s. Diffraction patterns of the samples were correlated with standard JCPDS data for its identification.

2.3. TEM

The microstructure of the particles was investigated by means of Transmission electron microscopy (TEM). The TEM images of the nanoparticles were recorded using a JEOL 4000EX High Resolution Transmission Electron Microscope (HRTEM) operated at 400 kV. The TEM images reveal the particle morphology and size of the nanopowder.

2.4. SEM

Scanning electron microscopy was used to investigate the surface morphology of the samples. SEM images of the samples were acquired with a scanning electron microscope (JSM-5600, JEOL Co., Japan). Samples were kept in a vacuum oven at
30°C overnight and were coated with a thin layer of gold by ion sputtering prior to microscopic examination. The energy dispersive analyzer was used for the elemental detection of the samples.

2.5. Ion exchange capacity

The ion exchange capacity (IEC) of the membranes, which is the amount of charged groups in the membrane, was measured using a titration method [1]. The ion exchange capacities (IECs) of the composite membranes were determined by double titration method. Samples were accurately weighed and were immersed in 25 ml of 0.05M HCl solution for 48 h and the HCl solution was back titrated by 0.05M NaOH solution using phenolphthalein as indicator. IECs of the samples were calculated using the equation:

\[
\text{IEC} = \frac{n_1 - n_2}{M_{\text{dry}}}
\]

Where \(n_1\) and \(n_2\) are the concentrations of (m mol) hydrochloric acid required before and after equilibrium respectively, and \(M_{\text{dry}}\) is the mass in g of the dried sample. The average value of the three samples calculated from the above equation is the IEC value of the membrane.

2.6. Thermo Gravimetric Analysis (TGA)

TGA thermograms of the membranes were recorded on a Shimadzu TGA-50H analyzer by heating the samples from room temperature to 850°C under nitrogen atmosphere at a heating rate of 10°C/min. This technique gives an indication of the short-term thermal properties and stabilities of the polymers.

2.7. Water uptake

Water uptake of the composite membranes was determined by weighing the membranes under wet conditions after being equilibrated in distilled water for 24 h at room temperature. The surfaces of the membranes were then carefully wiped with filter
paper and the membranes were weighed immediately. The samples were vacuum dried for two days and weighed again. The water uptake was calculated as follows [2].

\[
\text{Water uptake} \ (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \%
\]

Where \( W_{\text{wet}} \) is the mass of the water swollen membrane, and \( W_{\text{dry}} \) is the mass of the dry membrane.

### 2.8. Alkaline stability

The stability of the membranes in alkaline solution was examined by immersing the membrane samples in \( \text{N}_2 \) saturated 2M aq. NaOH at room temperature [3]. For this purpose, the membrane sample with a size of 3cm x 3cm was immersed in 2M aq. NaOH at room temperature for 2 weeks. They were taken out, washed with D.I. water, wiped with tissue paper, and then studied using FT-IR technique to detect any degradation or changes in chemical structures. Weight loss of the membrane is also recorded to detect their stability.

### 2.9. Oxidative stability

The oxidative stability of the membranes was tested by immersing the membranes in Fenton’s reagent (4 ppm FeSO\(_4\) in 3\% H\(_2\)O\(_2\)) for period of 24 h at room temperature. The membranes were intermittently taken out of the solution and weighed after wiping off the excess surface water. During this test membranes are subjected to free radical attack by OH\(^-\) and OOH\(^-\) formed by H\(_2\)O\(_2\) in the presence of Fe\(^{2+}\) and this may cause membrane degradation. Weight loss of the membranes was recorded to detect their stability [4,5].

### 2.10. Measurements of methanol permeability through membranes

The methanol permeability of the membranes was measured by Gasa’s method [6]. 20ml glass vials were filled with 10ml pure methanol. The membranes were clamped between the mouth of the vial and the cap. The cap had a 2cm x 2cm size hole so that the
methanol could escape only through the hole. The mass of the methanol inside the cell was measured as a function of time at room temperature. The methanol permeability (P) was calculated using the equation

\[ P = \frac{N \times d}{V \times P \times A \times t} \]

where \( N \) is the number of moles of methanol lost (moles), \( l \) is the thickness of the membrane (cm), \( P \) is the saturated vapor pressure of methanol, \( A \) is the area of the small hole on the cap (cm\(^2\)), and \( t \) is the time (days).

![Fig. 35 Cell for methanol permeability measurements](image)

### 2.11 Electrochemical impedance spectroscopy (EIS) techniques

Electrochemical impedance describes the response of a circuit to an alternating current or voltage as a function of frequency [7]. In DC circuit, only resistors resist the flow of current which is defined by Ohm's Law: \( E = I \times R \) where \( E \), \( I \) and \( R \) are potential, current and ohmic resistance respectively. While in an AC circuit, two other circuit elements, capacitors and inductors, impede the flow of electrons given by the analogous equation \( E = I \times Z \), where \( E \), \( I \) and \( Z \) are potential, current and impedance respectively. Impedance values are also measured in ohms. Impedance can be expressed as a complex
number, where the resistance is the real component and the combined capacitance and inductance is the imaginary component.

**Modeling of equivalent circuit**

An electrochemical cell has electrical double layers in the phase boundaries between interfaces of electrodes and electrolytes. This double layer has two opposite electric charges in the phase boundaries, which can be considered as a capacitor when we apply a low AC voltage [8].

![Interface diagram](image1)

**Fig. 36** The interface concept between the electrodes and the electrolyte [8]

![Equivalent circuit diagram](image2)

**Fig. 37** The equivalent circuit for measuring the membrane resistance [8]
An electrical circuit equivalent to this electrochemical system can be represented as above, where $R_{\text{sol}}$, $R_{\text{ct}}$, and $C_{\text{dl}}$ are the resistance of the solution, the charge transfer resistance, and the double layer capacitance. The charge transfer resistance is due to the difficulty of charge transfer on the surface of electrode. The double layer capacitance is the capacitance at the electrode surface. On applying an AC voltage $V$, to the capacitor

$$V = V_0 \exp(j2\pi ft)$$

Where $j$ is an imaginary unit, $f$ is frequency of the applied voltage, and $t$ time by second. The current $i$, can be written as

$$I = \frac{dQ}{dt} = C_{\text{dl}} \frac{dV}{dt} = (j2\pi f C_{\text{dl}}) E_0 \exp(j 2\pi f t) = (j 2\pi f C_{\text{dl}}) V$$

Where $Q$ stands for the total electrical charge passed. The impedance of the double layer $Z$ is

$$Z = \frac{V}{I} = \frac{1}{j(2\pi f C_{\text{dl}})}$$

The above equation shows that the impedance of an electrochemical system varies with applied frequency. For a circuit as in Fig. 37 the impedance is

$$Z = R_{\text{sol}} + \frac{R_{\text{ct}}}{1+j(2\pi f R_{\text{ct}} C_{\text{dl}})} = \left( R_{\text{sol}} + \frac{R_{\text{ct}}}{1+ (2\pi f R_{\text{ct}} C_{\text{dl}})^2} \right) - j\frac{2\pi f R_{\text{ct}}^2 C_{\text{dl}}}{1+ (2\pi f R_{\text{ct}} C_{\text{dl}})^2}$$

Above equation shows that imaginary part of impedance varies with the applied frequency. When the frequency increases toward infinity ($f \rightarrow \infty$), the impedance approximates the solution resistance ($R_{\text{sol}}$). When the frequency increases toward zero ($f \rightarrow 0$), the impedance approximates the sum of the solution resistant and the charge transfer resistance [8].
The Nyquist Plot

The EIS experiment involves applying a small sinusoidal voltage of about 10 mV and measuring the resulting current along with the phase angle [7]. Using this data, the real impedance component ($Z'$) and imaginary impedance components ($Z''$) are calculated and plotted against each other for varying frequencies in the Nyquist spectra [9]. The real impedance value ($Z'$) at the highest frequency measurement in the Nyquist plot was taken as the resistance of the membrane.

Ionic conductivity of the membranes was evaluated using AUTOLAB 50519 PGSTAT instrument. Impedance measurements of the membranes were performed in a two electrode setup where the membranes were clamped between two platinum electrodes and the cell was thermostated at 25±0.1°C for at least 20 minutes to ensure thermal equilibrium [10]. Impedance measurements were performed in the frequency range 100 Hz-1000 kHz using an alternating potential of amplitude 10 mV. Fully hydrated membranes were placed in the conductivity cell and it was filled with 1M NaOH. The real impedance value at the highest frequency measurement in the Nyquist plot was taken as the resistance of the membrane. This was then used to calculate the membrane conductivity. The resistance of the membrane and solution was measured ($R_{total}$) [8]. The resistance of the solution was measured without the membrane ($R_{solution}$). Membrane resistance ($R_{mem}$) was obtained from the difference of the measured resistances ($R_{mem} = R_{total} - R_{solution}$) [11]. The thickness of the membrane was measured with a digital micrometer by placing the membrane between two glass slides to ensure both a planar surface and limited compression. The conductivity of the membrane was calculated as follows $\sigma = \frac{L}{RA}$ mS cm$^{-1}$, Where $\sigma$ is the hydroxide conductivity in mS cm$^{-1}$, $R$ is the ohmic resistance of the membrane (Ω), L is the thickness of the membrane (in cm), A is the cross sectional area of membrane samples (cm$^2$).
Fig. 38 AUTOLAB 50519 PGSTAT instrument used for impedance measurements

Fig. 39 Conductivity cell used for the impedance measurements
2.12 Tensile strength measurements

Tensile testing is the most common methodology for the measurement of the tensile/mechanical strength of a material. The membrane samples were evaluated under a controlled strain rate until failure. The mechanical properties of the composite membranes were measured with universal testing machine (UTM) (Zwick, Model 1446-60, Germany). For this test the samples were prepared according to ASTM-D882 standard. The films were then placed between the grips of the testing machine. The grip length was 5cm and speed of testing was set at the rate of 10 mm min\(^{-1}\).

2.13 Performance of membranes as separator in all-iron flow battery

All-iron flow battery experiments were performed in the 36 cm\(^2\) flow cell hardware with electrolyte flowing across two electrodes, separated by the membrane prepared [12]. All experiments were performed with electrolyte flow rates of 25 ml min\(^{-1}\). Electrolyte for both positive and negative electrodes consisted of 1M FeCl\(_2\) and 1.5 M NH\(_4\)Cl. The electrodes were made from densified graphite with a cross-sectional area of 16 cm\(^2\). The charging efficiency of the all-iron redox flow cell was determined by Charging the cell at 100 mA cm\(^{-2}\) for 100 s followed by discharging at 50 mA cm\(^{-2}\) using AUTOLAB 50519 PGSTAT instrument. The cell performance is normally determined by its coulombic efficiency (CE). CE is the ratio of a cell’s discharge capacity (Q dis) to its charge capacity (Q ch).
Fig. 40 All-iron flow battery Schematic diagram
2.14 References


