



Bio-Composite Membrane Electrolytes for Direct Methanol Fuel Cells

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A new class of bio-composite polymer electrolyte membranes comprising chitosan (CS) and certain biomolecules in particular, plant hormones such as 3-indole acetic acid (IAA), 4-chlorophenoxy acetic acid (CAA) and 1-naphthalene acetic acid (NAA) are explored to realize proton-conducting bio-composite membranes for application in direct methanol fuel cells (DMFCs). The sorption capability, proton conductivity and ion-exchange capacity of the membranes are characterized in conjunction with their thermal and mechanical behaviour. A novel approach to measure the permeability of the membranes to both water and methanol is also reported, employing NMR imaging and volume localized NMR spectroscopy, using a two compartment permeability cell. A DMFC using CS-IAA composite membrane, operating with 2M aqueous methanol and air at 70°C delivers a peak power density of 25 mW/cm² at a load current density of 150 mA/cm². The study opens up the use of bio-compatible membranes in polymer-electrolyte-membrane fuel cells.

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Direct Methanol Fuel Cells (DMFCs) are promising candidate for automotive and portable power applications owing to their simplified system design, and high energy density of methanol, in addition to their easy handling.¹⁻³ During the last decade, the global market for DMFCs has grown and is expected to reach US\$ 2.6 billion by 2012. Such a trend has led to increasing demand for advanced materials and, in particular, for newer membranes so as to mitigate methanol crossover from anode to cathode in DMFCs, which causes conversion loss in terms of unaccounted fuel and depolarization loss due to the poisoning of the cathode electro-catalyst leading to substantial reduction in DMFC performance. Accordingly, it is desirable to develop solid polymer electrolyte membranes with low methanol diffusivities and appropriate proton conductivity. At present, perfluorosulfonic acid (PFSA)-based membranes find application in hydrogen fueled PEM fuel cells, but the use of these membranes in DMFCs requires structural modifications to mitigate methanol crossover.

In the literature,^{4,5} several polyelectrolytes have been proposed for DMFC applications with varying merits and demerits. The challenge in the development of alternative membrane electrolytes for DMFCs is to use cost effective materials with a balance between proton conductivity and methanol permeability.⁶⁻⁸ In this regard, the selection of polymer matrix and additives is essential as methanol permeability and proton conductivity largely depend on the properties of the polymer. For this purpose, an efficient alcohol/water separation membrane appears to be an appropriate material of choice. Natural polymers and their composite membranes are widely used for pervaporative separation of alcohol/water mixtures owing to their highly hydrophilic nature and selective affinity towards water.^{9,10} Pervaporation involves sorption of water molecules at the interface of the membrane, followed by diffusion across the membrane due to the concentration gradient and subsequent desorption into vapor phase. Accordingly, appropriate polymeric materials that would match the above characteristics are attractive base matrices to custom design a membrane electrolyte for DMFCs.

In recent years, interest in the naturally available class of polymers, known as polysaccharides, has been increasing rapidly and biopolymers are replacing synthetic polymers in several applications. Chitosan (CS) is a natural and low cost biopolymer with unique properties, such as bio-compatibility, nontoxicity, chemical and thermal stability, and has been widely studied as a promising membrane

material.^{11,12} CS is the second-most abundant natural biopolymer obtained by alkaline deacetylation of chitin, a major component of the exo-skeleton of crustaceans.¹³ Due to its low cost, natural abundance and eco-compatibility, CS has been a preferred membrane material for ultrafiltration, reverse osmosis, pervaporation and lithium ion batteries.¹⁴⁻¹⁷ Owing to the distinct advantages of excellent alcohol barrier and ion conducting properties, CS has also been studied as ion-exchange membranes.¹⁸⁻²⁰ In the literature,²¹⁻²⁶ different CS-based ion-exchange membranes, such as blend polyelectrolyte complex membranes and hybrid membranes comprising inorganic fillers, have been prepared and investigated for DMFC applications. The presence of both free amine and hydroxyl groups on the chitosan's backbone could facilitate improvement in its properties by complex formation through macromolecular systems since each of the nitrogen and oxygen atom in chitosan has a lone pair of electrons where complex formation can occur. Interestingly, studies on CS, sodium alginate (NaAlg) and polyvinyl alcohol (PVA)-based membranes have demonstrated restricted methanol crossover with successful use in DMFCs.²⁷⁻³¹ However, bio-composite membranes like CS, HEC, Gelatin have the advantage over synthetic membranes because of their environmentally benign properties in comparison to synthetic polymers.²⁷⁻³¹

In the present study, plant hormones (PH), which constitute one of the least explored classes of biomolecules owing to the diversity in their molecular structures and lesser understood biochemical pathways (unlike those in animal systems), are considered for fuel cell applications. These plant hormones are synthetically derived and based on the combination of physiological functions and molecular structure, plant hormones are broadly classified as auxins, cytokinins and gibberellins.³² As the objective of the present study is to augment the proton conductivity of CS polymer, selective hormones belonging to the auxin group involved in proton transport related process in biological systems are considered for constituting CS-PH bio-composite membranes, and are explored for their suitability in DMFCs. CS is also combined with either 3-indole acetic acid (IAA) or 4-chlorophenoxy acetic acid (CAA) and 1-naphthalene acetic acid (NAA) to pave the way for the deployment of bio-compatible natural products directly to improve the performance of DMFCs so as to address the associated issues of acid leaching. Spatially resolved NMR measurements of membrane permeability based on water or methanol release from a membrane ball to a suitable surrounding medium, as well as self-diffusion coefficients of water and methanol in membranes have been shown in our earlier work^{29-31,33} to reflect

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the performance of membranes in fuel cells. In this study, we report a novel two compartment permeability cell that allows membrane permeability measurements by spatially resolved NMR to be carried out directly on membrane sheets *ex situ* under osmotic drag conditions, resulting in excellent NMR sensitivity and highly reliable data.

Experimental

Membrane and electrode materials.— Chitosan (CS) with degree of deacetylation > 95%, 3-indole acetic acid (IAA), 4-chloro phenoxy acetic acid (CAA), 1-naphthalene acetic acid (NAA), and sulfosuccinic acid (70 wt.% in water) were procured from Sigma Aldrich chemicals. Glutaraldehyde (25 wt.% in water) was obtained from S. D. Fine Chemicals, India. Glacial acetic acid was procured from Rankem Chemicals, India. All chemicals were used as received. Toray TGP-H-120 carbon paper was obtained from Nikunj, India. Vulcan XC-72R carbon was procured from Cabot Corporation, US. Pt-Ru (60 wt. % in 1:1 atomic ratio) and Pt/C (40 wt.% Pt on Vulcan XC-72R carbon) were obtained from Alfa Aesar (Johnson Matthey). De-ionized (DI) water (18.4 MΩ cm) was produced by a Millipore system.

Membrane fabrication.— CS-PH bio-composite membranes were prepared by the solution-casting technique. In brief, 70 mL of 1 wt.% CS solution was obtained by dissolving the required amount of CS in 1 wt. % acetic acid at 30°C followed by stirring until a clear solution was obtained. A solution containing 0.3 mL of glutaraldehyde (GA) and 0.7 mL of sulfosuccinic acid (SSA) was added as a bi-crosslinker to the aqueous solution of CS. Similarly, 20 mL of 20 wt. % IAA in relation to CS was dissolved in 1 wt. % acetic acid followed by its stirring until a homogeneous solution was obtained. Both the solutions were mixed and stirred for 3–4 h to form a compatible composite solution. The above admixture was subjected to further stirring for 24 h. The admixtures were then transferred to flat Plexiglas plates and allowed to dry at room temperature (~30°C). CS-CAA and CS-NAA composite membranes were also prepared in a similar manner. CS membranes without addition of PHs were also prepared for comparison. Thickness of the pristine CS and composite membranes was ~170 μm. The thickness of the membrane was controlled by composition of the precursor solution. It may be noted that the precursor solution was spread on a glass plate of known area and the membranes were peeled after evaporating the solvent.

Ion-exchange capacity.— Ion-exchange capacity (IEC) indicates the number of milli equivalents of ions in 1 g of the membrane. To estimate IEC, membranes of similar weights (0.1 g) were soaked in 50 mL of 0.01N sodium hydroxide solutions for 12 h at room temperature (30°C) and 10 mL of the solution was titrated against 0.01N sulphuric acid.³⁴ IEC was estimated from Eq. 1

$$\text{IEC} = \frac{(B - P) \times 0.01 \times 5}{m} \quad [1]$$

In Eq. 1, IEC denotes the ion-exchange capacity (in meq/g); *B*, the amount of sulphuric acid used to neutralize blank sample solution in mL; and *P*, the amount of H₂SO₄ used to neutralize the membrane soaked solution in mL. The factor corresponding to the ratio of the amount of NaOH used to soak the mixed-matrix membrane to the amount used for titration is 5, and *m* denotes the membrane mass in g.

Water uptake and proton conductivity.— Water uptake measurements for CS and CS-PH bio-composite membranes were conducted by immersing the membrane samples in deionized water at room temperature for 24 h to attain equilibrium. Subsequently, the membranes were surface blotted with tissue paper, and weighed immediately on a microbalance (Sartorius, Germany) with an accuracy of ±0.01 mg. The samples were then dried in a hot air oven at 100°C for 12 h and their weights were measured. The % water uptake was calculated from

Eq. 2

$$\% \text{ water uptake} = \left(\frac{W_{\infty} - W_o}{W_o} \right) \times 100 \quad [2]$$

In Eq. 2, *W*_∞ and *W*_o refer to the weights of sorbed and dry membranes, respectively.

Proton conductivity measurements were performed on CS and CS-PH bio-composite membranes in a two-probe cell by ac impedance technique. The conductivity cell comprised two stainless steel electrodes, each of 20 mm diameter. The membrane sample was sandwiched between these two electrodes mounted in a Teflon block and kept in a closed glass container. The ionic conductivity data for the membranes were obtained under fully humidified condition (100% RH) by keeping deionized water at the bottom of the test container and equilibrating it for ~24 h. Subsequently, conductivity measurements were conducted between 30°C and 100°C in a glass container with the provision to heat. The temperature was constantly monitored with a thermometer kept inside the container adjacent to the membrane. AC impedance data for the membranes were obtained in the frequency range between 1 MHz and 1 Hz with 10 mV amplitude using an Autolab PGSTAT 30. The resistance (*R*) of the membrane was determined from the high-frequency intercept of the impedance with the real axis and the membrane conductivity was calculated from Eq. 3

$$\sigma = \frac{l}{RA} \quad [3]$$

In Eq. 3, *σ* is the proton conductivity of the membrane in S/cm, *l* is the membrane thickness in centimeter and *A* is the membrane cross-sectional area in cm².

Thermal and mechanical characterization.— Thermo gravimetric analysis for all the membranes was carried out using an SDT Q600 V8.2 TGA/DTA instrument in the temperature range between 30°C and 700°C at a heating rate of 5°C/min with nitrogen flushed at 200 mL/min. Universal testing machine (UTM/Model AGS-J, Shimadzu) with an operating head load of 10 kN was used to study the mechanical properties of the membranes. Cross-sectional area of the sample was obtained from the width and thickness of the membrane sample. The test samples were prepared in the form of dumb bell shaped objects as per ASTM D-882 standards. The membranes were then placed in the sample holder of the machine. The film was stretched at a cross-head speed of 1 mm/min and its tensile strength was estimated from Eq. 4

$$\text{Tensile strength (MPa)} = \frac{\text{Maximum load}}{\text{Cross - sectional area}} \quad [4]$$

Spatially resolved NMR characterization.— **Membrane permeability to water/methanol.**— A permeability cell was designed, comprising two independent compartments made of Plexiglas, each with a volume of about 15 mL. Each compartment rests on a pod on one end, and a flange on the open end. The two compartments are together to constitute the whole cell by screwing together the flanges with Teflon screws and nuts, using fiber glass reinforced Teflon gaskets. The approximate outer dimensions of the assembled two compartment cell are: 7.6 cm × 3 cm × 3.1 cm, resting on pods of height 1.5 cm. The membrane sheet, cut to the size of the open end of the compartments, is inserted between the two gaskets. Both the compartments are filled simultaneously with equal amounts of the respective liquids –15 mL each in this case, and placed inside the NMR resonator. The experiments reported here were carried out on a Bruker Biospec 47/40 system operating at 200 MHz, employing a 112/72 ¹H resonator.

Water permeation kinetics studies were carried out by filling one compartment of the permeability cell with water and the other with D₂O, the compartments being separated by a sheet of the membrane to be characterized. Gradient echo imaging helps monitor the water concentration changes in both the compartments simultaneously, with

rapid image acquisition. The first measurement is typically initiated 10–15 minutes after filling the compartments and completing the setup procedure. A series of 128×128 coronal images were acquired at different time intervals with a 1 mm slice thickness, 4.21 ms echo time (TE) and 300 ms repetition time (TR). Other relevant image parameters were: 30° pulse flip angle, 9 cm field of view (FOV) in the read direction and 3 cm FOV in the phase encode direction, the number of averages (NA) being 4.

Methanol permeation studies were undertaken in volume localized spectral mode. It is to be noted that owing to the relatively low concentration of methanol in water, selective NMR imaging of methanol is not very practical, except at high fields, in view of the fact that the chemical shift difference between H_2O and the methyl group of CH_3OH is only about 1.5 ppm. Furthermore, the direct imaging of species at low concentration imposes limitations on time course studies, since sensitivity is effectively reduced in the presence of the read gradient required for imaging, regardless of the field of operation. On the other hand, volume selective high resolution spectroscopy offers an opportunity to track the process of methanol release, employing outer volume suppression, as well as water suppression in the voxel of interest. In this high resolution scenario, a 1.5 ppm chemical shift difference is now a convenient handle to readily distinguish the species of interest.

Methanol release kinetics was studied by filling one compartment with 2M CH_3OH in water and the other with water, thereby mimicking the situation in the actual fuel cell. The experimental strategy was to acquire the volume localized high resolution ^1H NMR spectrum from a fixed volume element in the water compartment as a function of time, the voxel chosen being a cube of edge 4 mm. The horizontal distance along the field direction, z , from the membrane to the center of the voxel was *ca.* 2.4 cm in each case. The volume localization protocol employed was 'point resolved spectroscopy' (PRESS),³⁵ the other relevant experimental parameters being: TR: 2500 ms, TE: 13.4 ms, spectral width (SW): 10 ppm and NA: 32. Water suppression was carried out using the variable power and optimized relaxation delays sequence, VAPOR, with 150 Hz bandwidth.

Water/methanol self-diffusion within the membrane.— NMR self-diffusion measurements were carried out on a Bruker Avance II 500 MHz wide bore system equipped with a 5 mm diffusion probe, permitting a maximum z -gradient amplitude of about 18 T m^{-1} . The self-diffusion coefficient was determined by the NMR pulsed field gradient stimulated echo (PGSTE) technique. For water diffusion measurements the membranes were equilibrated in water, cut into small pieces of *ca.* 3 mm $\times$ 1 cm area, and inserted into an NMR tube after surface blotting. The relevant experimental parameters were: spectral width (SWH): 11433 Hz, relaxation delay: 30 s (delay from start of data acquisition to start of next scan, i.e., $d1+aq$), 1024 time domain data points (TD), and 4 scans. For methanol diffusion studies the membranes, cut to a similar size as before, were equilibrated in 2M CH_3OH in D_2O and the relevant experimental parameters were: SWH: 13021 Hz, $d1+aq$: 60 s, TD: 1024, and 4 scans.

The diffusion experiment was performed as a function of gradient amplitude. The standard fit equation was employed to obtain the self-diffusion coefficient (D):

$$I(g) = I(0) \exp \left(-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right) \quad [5]$$

In Eq. 5, $I(g)$ is the signal intensity that results for a gradient amplitude g , $I(0)$ is the signal intensity that results when the gradient is off, γ is the magnetogyric ratio of the observed nucleus, δ is the 'rectangular' gradient pulse duration (typically 1 ms) and Δ is the time interval between the two gradient pulses (start-to-start) that encode and decode the diffusion.

Single-cell assembly and DMFC performance.— The performance of CS and CS-PH bio-composite membranes were evaluated in

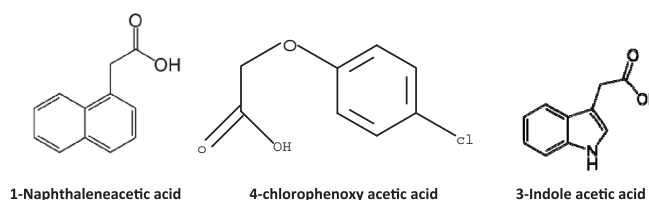


Figure 1. Molecular structures for plant hormones used in the present study: (a) 1-naphthalene acetic acid (NAA) (b) 4-chlorophenoxy acetic acid (CAA), and (c) 3-indole acetic acid (IAA).

a DMFC by making membrane electrode assemblies (MEAs). In brief, both the anode and cathode comprised a backing layer, a gas diffusion layer (GDL) and a reaction layer. Teflonised Toray carbon papers (thickness = 0.38 mm) were employed as the backing layers for these electrodes. Diffusion layer comprising 1.5 mg/cm^2 of Vulcan XC-72R carbon slurry dispersed in cyclohexane was applied onto the backing layers followed by sintering in a muffle furnace at 350°C for 30 min. 60 wt.% Pt-Ru (1:1 atomic ratio) supported on Vulcan XC-72R carbon mixed with Nafion ionomer and coated on to one of the GDLs constituted the catalyst layer on the anode, while 40 wt.% Pt catalyst supported on Vulcan XC-72R carbon mixed with Nafion ionomer coated on to the other GDL constituted the catalyst layer on the cathode. The catalyst loading on both the anode and cathode was kept at 2 mg/cm^2 . The active area for the DMFC was 4 cm^2 . MEAs comprising CS and CS-PH bio-composite membranes were obtained by hot pressing at 15 kN ($\sim 60 \text{ kg/cm}^2$) at 80°C for 2 min. MEAs were evaluated using a conventional fuel cell fixture with parallel serpentine flow field machined on graphite plates. The cells were tested at 70°C with 2M aqueous methanol at a flow rate of 2 mL/min at the anode side and air at the cathode side at a flow rate of 300 mL/min at atmospheric pressure. Cell voltage and current density in relation to power density were measured galvanostatically using an Arbin Fuel Cell Test Station (Model PEM-FCTS-158541).

Results and Discussion

Ion-exchange capacity (IEC) of membranes.— Plant hormones structurally shown in Fig. 1 are used for realizing CS-PH bio-composite membranes. IEC is an indication of the ion-exchangeable groups present in a polymeric matrix responsible for the proton conduction and thus provides an indirect but reliable approximation for proton conduction. The measured IEC values are 0.58 meq./g, 0.51 meq./g and 0.43 meq./g for CS-IAA, CS-CAA and CS-NAA bio-composite membranes, respectively. However, for CS membrane, the IEC value is 0.29 meq./g, which is lower than the other membranes aforesaid, suggesting the poor proton dissociation ability for CS membrane. Incorporation of PH leads to significant increase in IEC values owing to the increase in the ionic groups present in the bio-composite membrane.

Water uptake and proton conductivity of membranes.— It is generally accepted that the water uptake behavior has an intense influence on both stability and proton conductance of polymer electrolyte membrane. Proton transport requires a significant amount of water to coordinate with protons. However, excessive water uptake will result in dimensional change of membranes, and introduce large humidity induced stress in the membrane.^{36–38} Water uptake values for CS and CS-PH bio-composite membranes are given in Table I. Tendency towards the enhanced uptake of water molecules after the addition of PH clearly demonstrates the interaction of CS polymeric chains with the PH molecules. CS-IAA bio-composite exhibits higher water uptake than CS-CAA and CS-NAA bio-composites. As water uptake increases, the proton conductivity is enhanced due to increase in mobility of ions.

Table I. Physico-chemical properties of the CS and CS-PH bio-composite membranes.

Membrane types	Water uptake (%)	Ion exchange capacity (meq./g)	Activation energy (kJ/mol)	Tensile strength (MPa)	Elongation at break (%)
CS	40.9	0.29	25.71	6.6	10.2
CS-IAA	56.5	0.58	33.48	14.1	12
CS-NAA	52.8	0.43	35.91	11.5	10.8
CS-CAA	53.2	0.51	43.08	9.6	8.1

Proton conductivity for CS and CS-PH bio-composite membranes increases with increasing temperature. The proton conductivity of bio-composite membranes is higher in relation to the CS membrane. Higher proton conductivity of bio-composite membranes is probably due to the proton accepting nature of the hormone molecules and the formation of zwitter ionic architecture in the CS-PH membranes created by acid-base interactions and hydrogen bonding. It is conjectured that the original structural arrangement for the CS polymer chains is altered in presence of PH and their strong affinity towards the water molecules leads to hydrophilic regions in the polymer matrix. These hydrophilic regions formed around the polymer chains result in higher water uptake with consequent increase in the proton conduction by forming facile channels for proton transport.³⁹

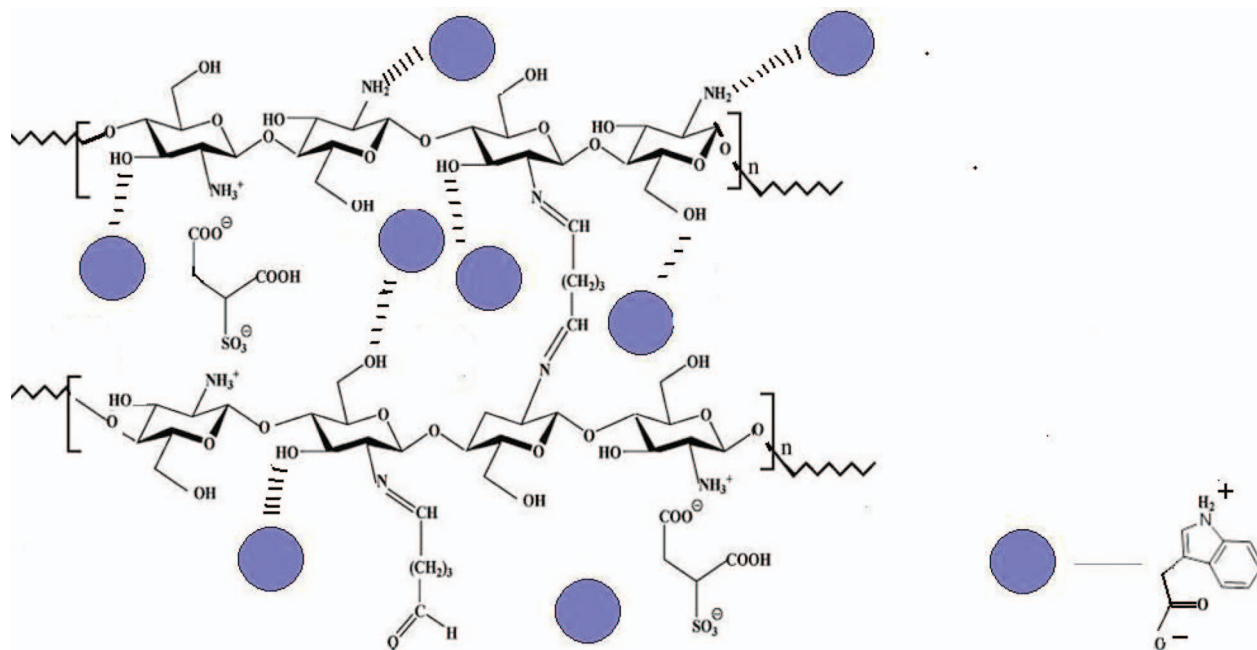
The variation in conductivity as a function of temperature follows the Arrhenius relation as shown in Fig. 2. All the membranes exhibit an Arrhenius-type temperature dependence of proton conductivity implying thermally activated process. With increasing temperature, the proton conductivity values for bio-composite membranes are found to be higher in relation to CS membrane, probably due to the presence of more bound water in the composites. The activation energy, which is the energy required for proton transport, is calculated from the slope of Arrhenius plots obtained by plotting $\ln \sigma$ vs. $1/T$ according to Eq. 6 given below

$$\sigma = \sigma_0 e^{-(E_a/RT)} \quad [6]$$

In Eq. 6, σ is the proton conductivity in S/cm, σ_0 is the pre-exponential factor, E_a is the activation energy in kJ/mol, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

E_a values for CS-PH bio-composite membranes are higher (33–43 kJ/mol) than the E_a value (25.71 kJ/mol) for CS membrane. In other words, the E_a for proton conduction increases with the introduction of PH moiety into the CS matrix. According to the vehicular mechanism,⁴⁰ CS-PH bio-composite membranes hold higher number of water molecules and are attached by means of hydrogen bond to the composites.

Mechanical stability of membranes.— The effect of incorporation of PH on the mechanical properties of the membrane is studied for determining the tensile strength and the percentage elongation at break, and the data are presented in Table I. The tensile strength for CS membrane increases on addition of PH due to the strong interaction of PH with CS matrix. It is likely that the zwitter ions of the plant hormone interact with either -OH or -NH₂ group present in CS as shown in Scheme 1. The tensile strength and percentage elongation for CS-IAA bio-composite membrane are higher than CS, CS-NAA and CS-CAA, reflecting higher chain flexibility of the matrix for the former. It is noteworthy that for CS-NAA and CS-CAA, % elongation is reduced due to the higher membrane rigidity compared to CS-IAA bio-composite membrane.

**Scheme 1.** Interaction of plant hormones (IAA) with binary cross-linked (GA + SSA) CS network.

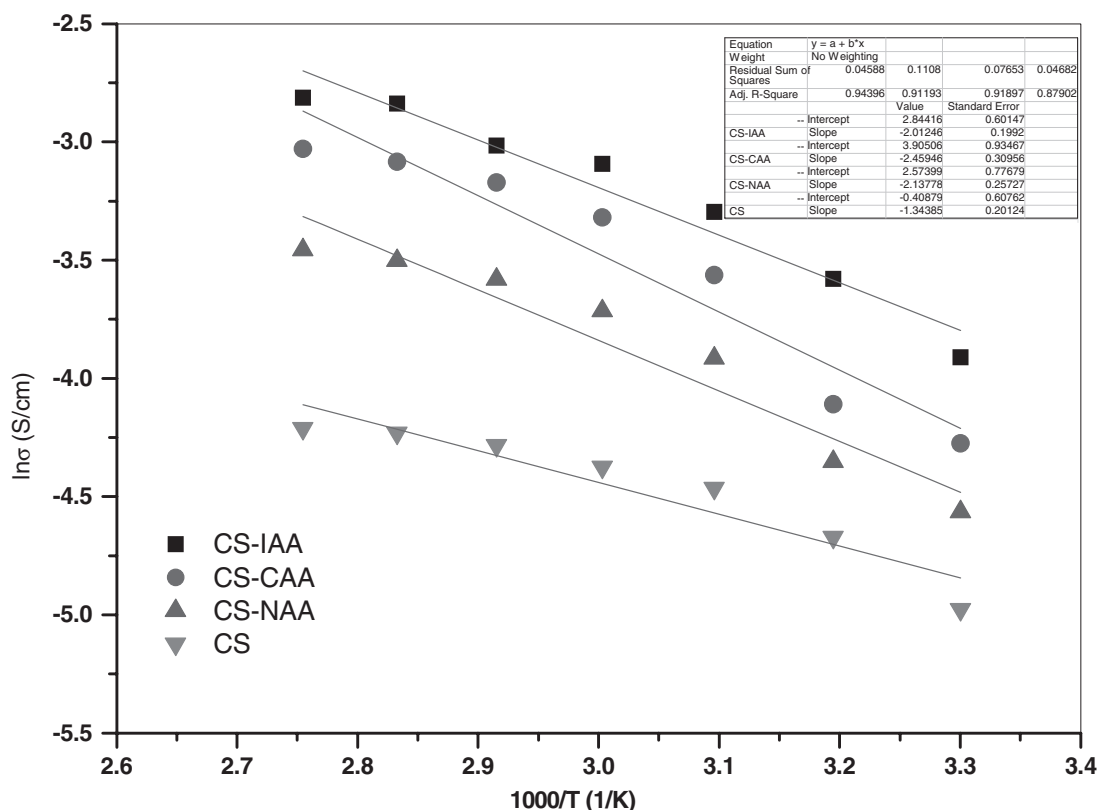


Figure 2. $\ln \sigma$ vs. $1000/T$ plot for CS, CS-IAA, CS-CAA and CS-NAA bio-composite membranes.

Thermo gravimetric analysis of membranes.— TGA data for CS membrane and CS-PH bio-composite membranes are shown in Fig. 3. The weight loss for all samples below 150°C is mainly due to the physically absorbed water molecules. It is noteworthy that the weight loss for CS membrane is higher in relation to CS-PH bio-composite membrane. The weight loss for CS-NAA bio-composite membrane is lowest, while the weight loss for CS-IAA and CS-CAA is intermediate to that for CS and CS-NAA bio-composite membranes. This indicates the presence of more bound water in bio-composite membranes in relation to the CS membrane. The weight loss be-

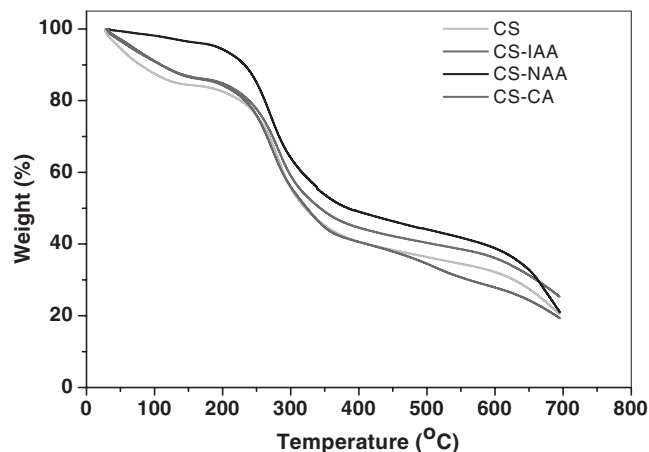


Figure 3. TGA plots for (a) CS (b) CS-IAA (c) CS-CAA and (d) CS-NAA bio-composite membranes.

tween 150°C and 360°C could be due to the decomposition of chitosan and the vaporization of volatile products.¹⁴ On comparing the thermograms of CS membrane and CS-PH bio-composites, it is evident that the thermal properties of CS are enhanced on addition of PH. There is only a marginal difference in the thermal behavior primarily because the base matrix happens to be the same in all the cases.

Spatially resolved NMR characterization.— **Membrane permeability to water and methanol.**— Water permeation through the membrane, from the water compartment to the D_2O compartment is recorded at different time intervals by gradient echo imaging; some gradient echo images obtained at different points of time after start of the experiment are presented in Fig. 4 for a representative membrane. The kinetics data culled from the image analysis are presented in Figs. 5a–5j and summarized in Table II. The equation used for fitting the curve is:

$$I(t) = I(\infty) + A_1 \exp(-kt) \quad [7]$$

In Eq. 7, $I(\infty)$ and $I(t)$ are mean signal intensities of water at infinite time (i.e., the asymptotic value) and at time ' t ' respectively, while k is the rate constant and A_1 is the difference between the initial signal intensity ($I(0)$) and the asymptotic signal intensity ($I(\infty)$).

The mean signal intensity of water from a chosen ROI (Region of Interest) from both compartments was plotted as a function of time. This quantity exhibits an exponential decay in the water compartment and an exponential growth in the D_2O compartment. From these measurements, the membrane with the plant hormone IAA is inferred to have the highest water permeability.

Methanol permeation through the membrane, from the 2M CH_3OH compartment to the water compartment was also recorded at different time intervals by volume localized spectroscopy. The

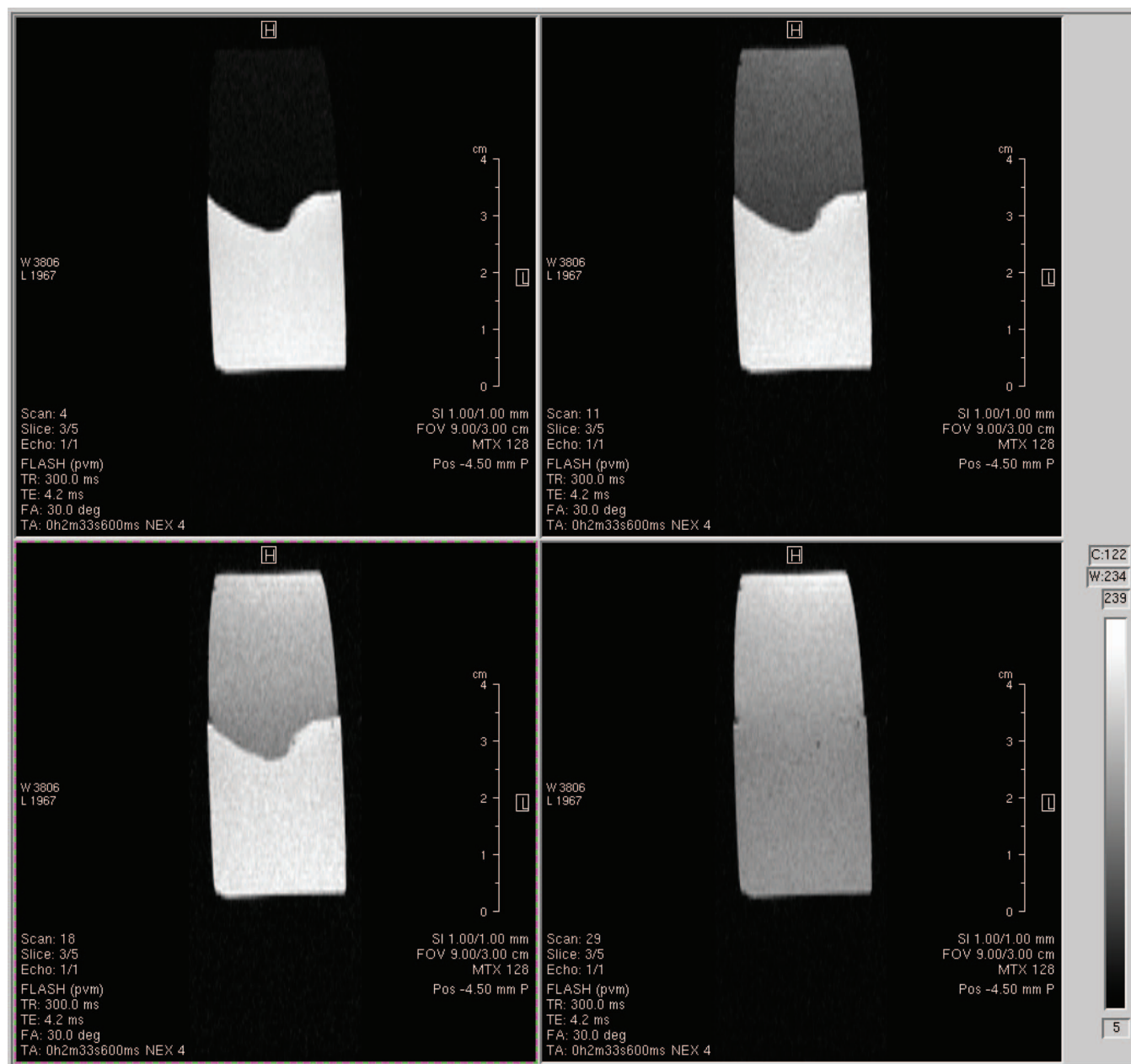


Figure 4. NMR images for study of permeability to water. From left to right, top to bottom: obtained 19, 55, 97 and 282 minutes after filling the two compartments of the cell with CS-IAA membrane as the separator.

Table II. Water permeability data measured by gradient echo NMR imaging.

Membrane	$k \times 10^3 \text{ (min}^{-1}\text{)}$ H ₂ O comp.	$k \times 10^3 \text{ (min}^{-1}\text{)}$ D ₂ O comp.
CS-IAA	18.15 ± 0.05	15.06 ± 0.25
CS-NAA	16.30 ± 0.07	11.69 ± 0.38
CS	14.51 ± 0.04	10.64 ± 0.33
CS-CAA	13.62 ± 0.06	9.84 ± 0.34
Nafion	2.49 ± 0.07	1.9 ± 0.17

kinetics data are culled from the integral of the methyl peak in the volume localized ^1H spectra; stack plots of the spectra are presented in Fig. 6a–6e. The integrals $I(t)$ as a function of time are then fitted to an exponential function of the form of Eq. 7. Figs. 7a–7e show the resulting plots and the results are summarized in Table III.

It may be noted that the rate constants measured respectively for water and methanol transport across the membranes by gradient echo imaging and MRS comprise a contribution from the permeation of the respective molecular species across the membrane as also a contribution from the diffusion of these species through the bulk medium beyond the membrane. The contribution to the observed rate from this diffusion process in the bulk medium cannot be neglected as stirring or mixing of the solution is not effected. Instead, sampling is done entirely non-invasively. In order to compare

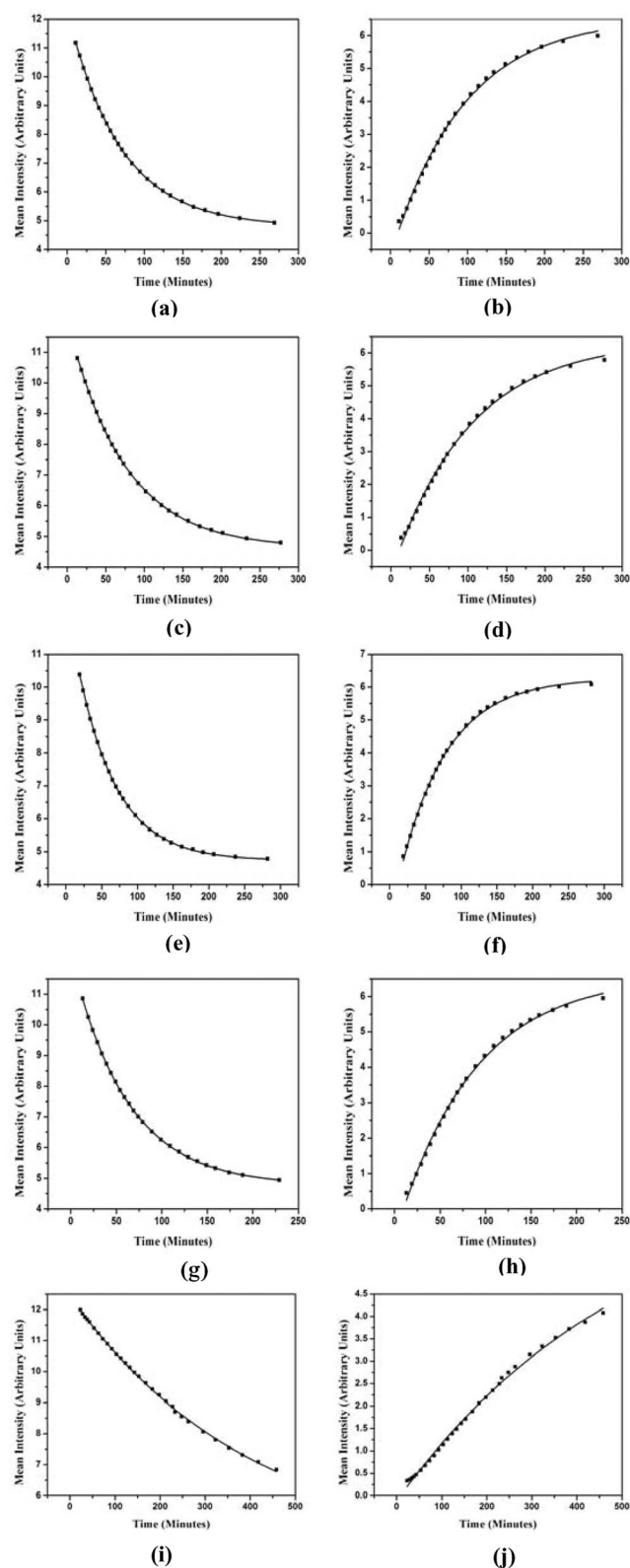


Figure 5. Water permeability of CS, CS-CAA, CS-IAA, CS-NAA and Nafion; mean signal intensity from the chosen ROI in the water compartment is plotted in a, c, e, g and i respectively, while b, d, f, h and j represent this quantity measured in the D₂O compartment. All the plots are fitted with an exponential equation: $I(t) = I(\infty) + A_1 \exp(-kt)$.

Table III. Methanol permeability data measured by volume localized NMR spectroscopy.

Membrane	$k \times 10^3 \text{ (min}^{-1}\text{)}$	A_1	$I(\infty)$	R^2
CS-IAA	5.51 ± 0.09	-17.46 ± 0.109	15.99 ± 0.135	0.99978
CS-CAA	4.54 ± 0.07	-16.90 ± 0.125	15.97 ± 0.147	0.99980
CS-NAA	5.23 ± 0.07	-16.35 ± 0.088	15.25 ± 0.109	0.99984
CS	6.07 ± 0.11	-15.44 ± 0.095	14.44 ± 0.12	0.99957
Nafion	4.02 ± 0.06	-16.01 ± 0.114	15.09 ± 0.131	0.99982

membrane permeabilities, therefore, data were collected from a region of the sample at a fixed distance from the membrane for all systems investigated. It may be noted further that sampling was not done close to the membrane, in order to avoid magnetic susceptibility gradient effects. Since the molecular species, the medium and the distance of travel of the molecular species in the medium are all constant, the only variable being the membrane itself, comparison of the observed rates directly reflects the differences in membrane permeability.

It is clearly seen from Table III that methanol permeability for bio-composite membranes is comparable to Nafion. However, although water permeability for bio-composite membranes is almost one order higher than that for Nafion as given in Table II, the ionic conductivity values for former are lower than the latter due to the fact that the ion exchange capacity for bio-composite membranes are about four times lesser than Nafion.

Water/methanol self-diffusion coefficients within the membrane.— NMR self-diffusion coefficients obtained from PGSTE measurements are given in Table IV. Water self-diffusion coefficient is found to be highest for the CS-IAA membrane whereas the CS-NAA membrane shows the highest methanol self-diffusion coefficient. Due to the large linewidth, the water self-diffusion coefficient could not be measured for the CS membrane.

DMFC performance studies.— The performance of membranes for DMFC is evaluated by considering both the proton conductivity and methanol permeability. However, the realistic approach to determine membrane suitability in DMFC is testing it in fuel cell mode. Figure 8 shows the DMFC performance curves for MEAs comprising Nafion-117, CS membrane and CS-PH bio-composite membranes at 70°C under atmospheric pressure. The peak power density for CS membrane is about 11 mW/cm² at a load current density of 100 mA/cm². In contrast, the performance of DMFCs increases on addition of PHs to CS matrix. This is due to the increase in the proton conductivity of the CS-PH bio-composite membranes. The CS-IAA bio-composite membrane shows better DMFC performance in relation to other bio-composite membranes. A peak power density of 25 mW/cm² at load current density of 150 mA/cm² is observed for the DMFC incorporating CS-IAA bio-composite membrane; while peak power density values of 18 mW/cm² and 16 mW/cm² at load current-density of 130 mA/cm² and 115 mA/cm² are observed for the DMFCs incorporating CS-CAA and CS-NAA, respectively. The high activation overpotential observed (Fig. 8) for CS and CS-NAA membranes are due to higher methanol crossover as compared to CS-IAA and CS-CAA. These data are in conformity with the proton conductivity data. However, the DMFC performance of all the membranes is lower in relation to Nafion-117 membrane. It is to be noted that the membranes reported in the study does utilize free acid, unlike Nafion and other sulfonated membranes, and the possibility of acid leaching over prolonged usage of the membrane is highly likely.

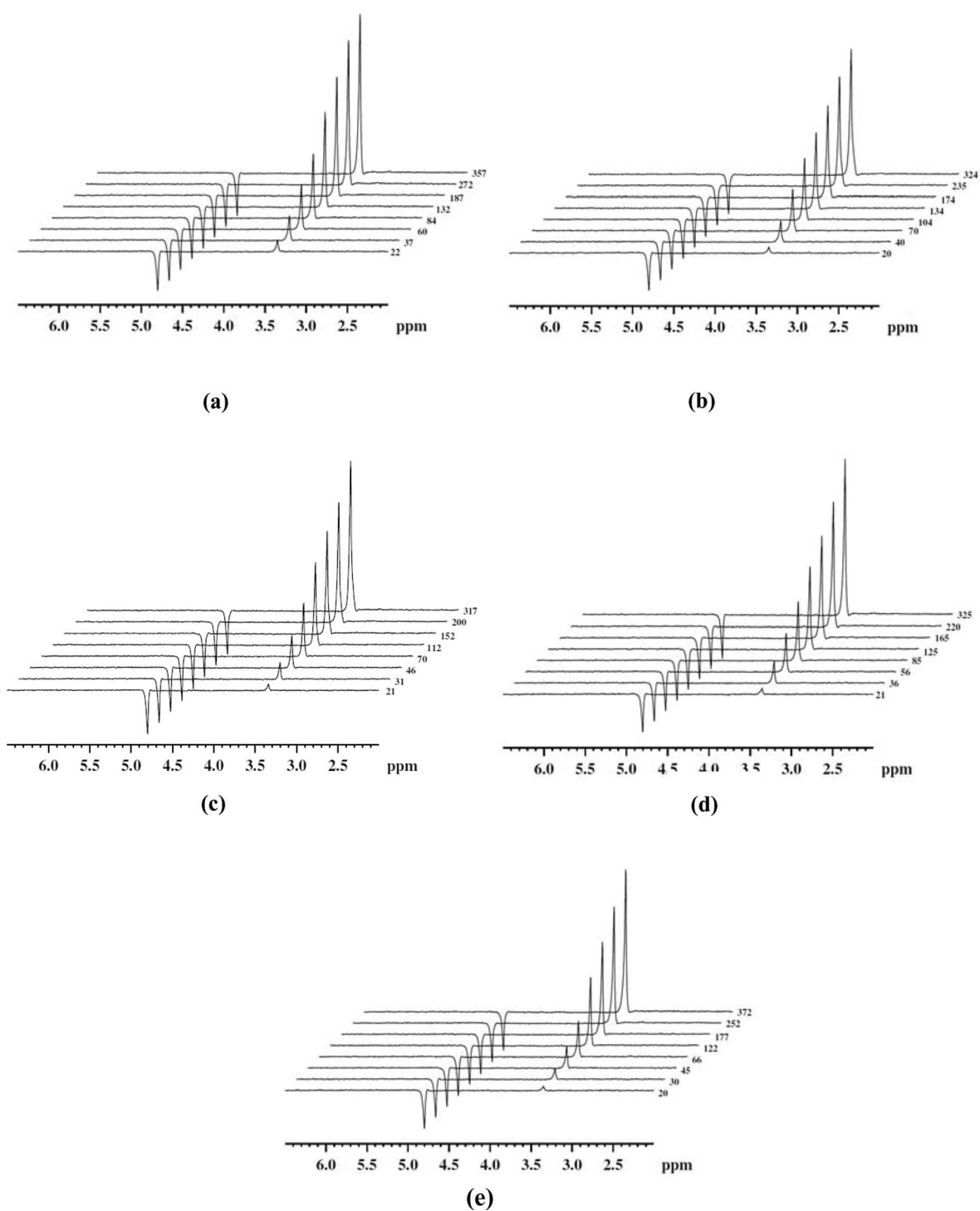


Figure 6. Volume localized spectra for measurement of methanol permeability: (a) CS; (b) CS-CAA; (c) CS-IAA; (d) CS-NAA and (e) Nafion. The time in minutes at which each measurement commenced after filling the permeability cell is indicated to the right of each spectral trace.

Table IV. Apparent self-diffusion coefficients of water and methanol measured by PGSTE. ($\Delta = 5.17\text{--}5.2$ ms)

Species	CS $D \times 10^{10}$ (m ² /s)	CS-CAA $D \times 10^{10}$ (m ² /s)	CS-IAA $D \times 10^{10}$ (m ² /s)	CS-NAA $D \times 10^{10}$ (m ² /s)
Water	—	4.896	13.61	11.75
Methanol	3.31	6.981	6.39	7.588

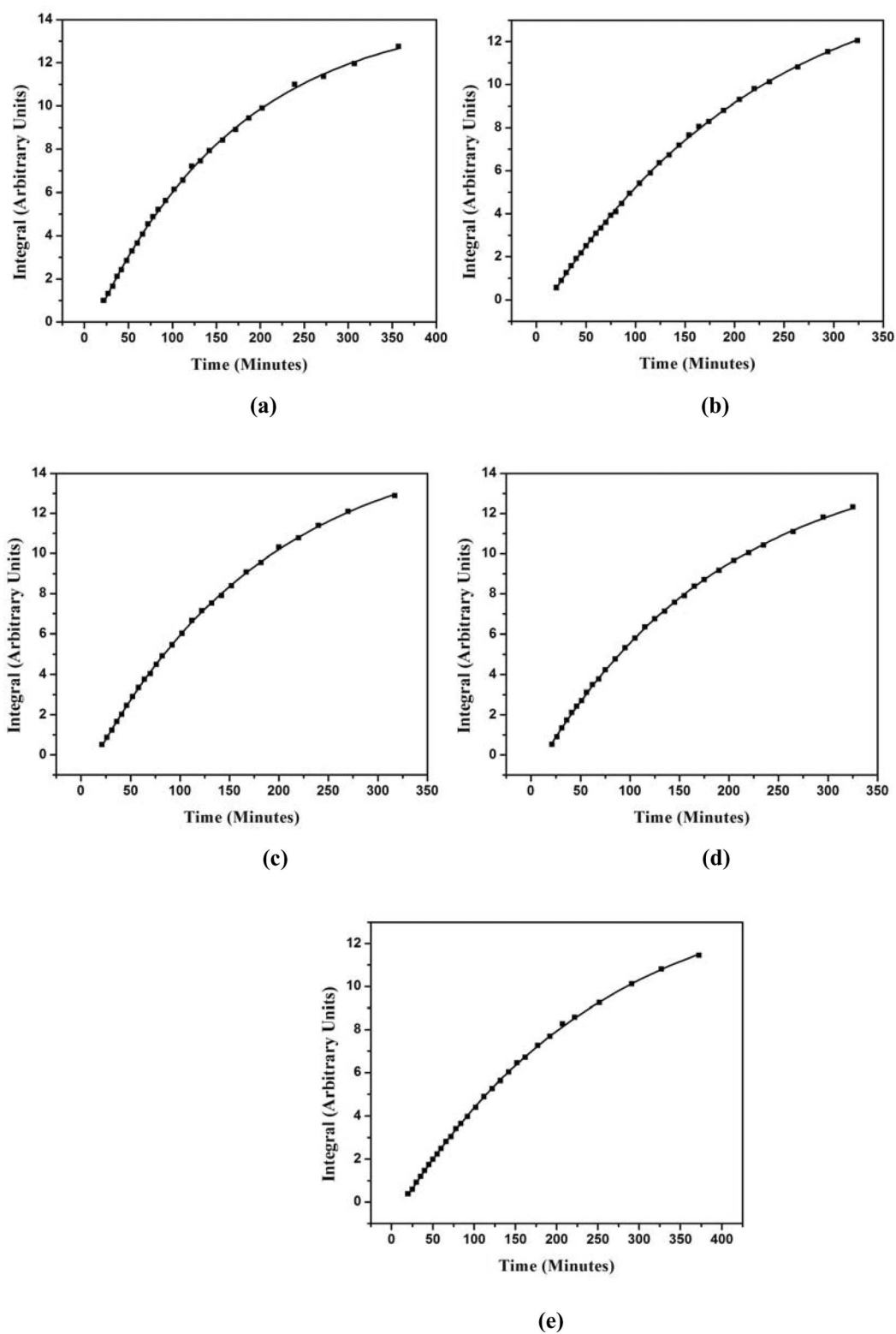


Figure 7. Plots for the integral of the methyl signal of methanol vs. time for four different membranes: (a) CS; (b) CS-CAA; (c) CS-IAA; (d) CS-NAA; and (e) Nafion. All the plots are fitted with an exponential equation: $I(t) = I(\infty) + A_1 \exp(-kt)$.

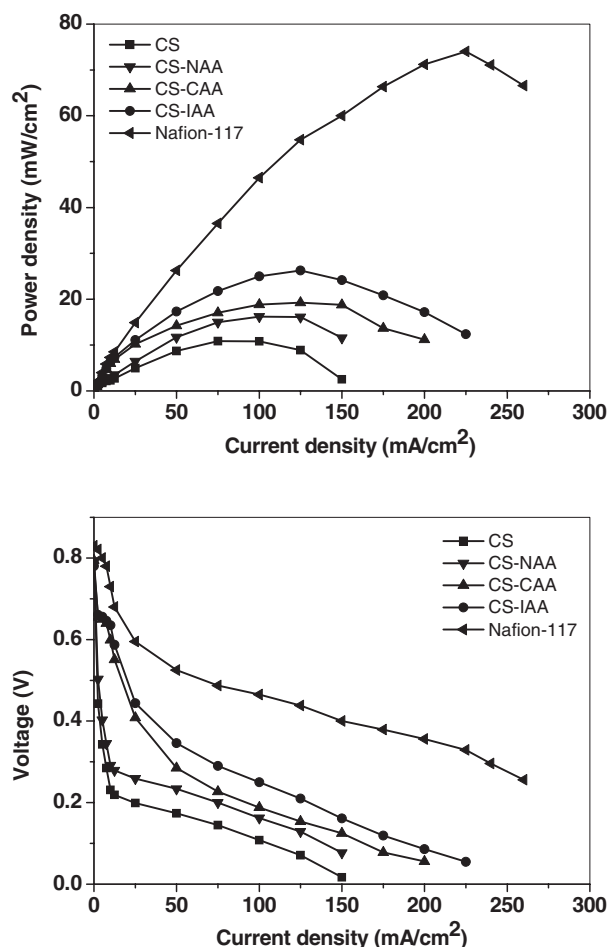


Figure 8. (a) Cell voltage and (b) power density vs. current-density data for DMFCs operating with CS, CS-IAA, CS-CAA and CS-NAA bio-composite membranes at 70°C.

Conclusions

Bio-composites comprising a natural polymer and plant hormones are prepared and evaluated as proton conducting membrane electrolytes for DMFCs. It is demonstrated that membrane morphology could be tuned with biomolecules for limiting methanol permeation across the membrane. Permeability studies on these membranes have been carried out with high reliability employing NMR imaging and volume localized spectroscopy, using a two compartment permeability cell. Regardless of the peak power densities, these bio-composites possess several attractive features such as convenient method of preparation, low cost, good thermal stability as well as recycling potential unlike commercially available membranes. Accordingly, the study opens up the possibility of using cost-effective bio-compatible membranes in DMFCs.

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