

Short communication

Carbon nanotubes rooted montmorillonite (CNT-MM) reinforced nanocomposite membrane for PEM fuel cells

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ABSTRACT

Nafion based nanocomposite membranes containing montmorillonite-carbon nanotubes (a binary hybrid material) were produced to develop high performance polymer electrolyte fuel cells. Multi walled carbon nanotubes were grown over 20 and 25 wt% iron loaded montmorillonite catalysts by CVD using acetylene as the carbon precursor. Growth experiments were carried out at optimised conditions to obtain highly selective crystalline carbon nanotubes. X-ray diffraction spectra of the catalysts were recorded for the structural characterisation and definition of particle size. The carbon nanotubes obtained were examined by various physico chemical characterisation studies such as SEM, TEM, Raman spectroscopy and TG analyses to understand the morphology and crystallinity of the CNTs. The MM-CNT hybrid material with I_D/I_G ratio of Raman spectral band as 0.53 represents the high selectivity towards CNTs. Thus the hybrid material produced was considered as the best nanofiller to develop polymer nanocomposites. Nafion based nanocomposite membranes were prepared by adding MM-CNT as nanofiller by solution casting method. A better dispersion of MM-CNT into the Nafion matrix was observed and the addition of the MM-CNT improved the thermal stability of the Nafion membrane.

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1. Introduction

Fuel cells are considered to be the promising alternative power source of next generation because of the depletion of fossil fuels and of avoiding the environmental pollution from the toxic emissions. Efficiencies up to 60% and higher energy densities relative to batteries are very significant advantages to use fuel cells for numerous applications such as automobiles, portable electronic devices and for mobile stationary power generation [1–5]. Fuel cell is one of the most significant areas that reach good heights of research and development during the past two decades [6–10]. Particularly proton exchange membrane (PEM) fuel cells are very attractive for domestic and automobile applications because of their low construction cost, low operating temperature and high efficiency compared to other fuel cells.

A PEM fuel cell uses a polymer membrane as an electrolyte which conducts protons to the cathode side. The most commonly used membrane called Nafion is a perfluoro sulphonyl fluoride

copolymer from DuPont. Although Nafion is the most desirable candidate for the fabrication of fuel cell membrane, it has few drawbacks such as low conductivity at low humidity and/or high temperature ($>100^\circ\text{C}$), loss of mechanical stability at high temperature ($\geq 100^\circ\text{C}$), elevated methanol permeability and restricted operation temperature. The higher methanol permeability should be avoided to achieve high efficiency and to protect the cathode. Electrolyte membranes of high proton conductivity (0.01 S cm^{-1}) and no dependence on humidity at above 100°C are very desirable because high temperature disfavours the CO poisoning of the electrode catalysts made of platinum. Recently many efforts have been made to develop Nafion based nanocomposite membranes to overcome the above mentioned disadvantages. Mainly carbon nanotubes (one dimensional), clay (two dimensional), silica and other inorganic nanoparticles (three dimensional) were incorporated into the Nafion matrix for the preparation of high temperature PEMs [6–10].

Clay reinforced Nafion nanocomposite membranes have been extensively developed with high mechanical strength and thermal stability [11–16]. Similarly, carbon nanotubes added Nafion nanocomposite membranes of good mechanical stability with reduced methanol permeability and increased ionic conductivity were also reported [17–19]. But still the homogeneous dispersion

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of the carbon nanotubes (CNTs) in the Nafion matrix is a big challenging issue. From the literature it is well understood that both the nanofillers such as clay and CNTs individually improve the mechanical and thermal stability of the resulting nanocomposite membranes. Also it is very clear that the filler should have a synergistic effect between ionic conductivity (C) and methanol permeability (P). The better performance of PEM could be obtained when C/P ratio is kept as high, which means that the filler should lower the methanol permeability of the composite membrane with increase in ionic conductivity.

In this frame, it is expected that the synergistic action of clay-carbon nanotubes in Nafion matrix would provide outstanding functionalities to the resulting composite membrane. Thus in the current investigation we have developed new hybrid material by chemical vapour deposition (CVD) which contains montmorillonite and carbon nanotubes together (MM-CNT) and fabricated Nafion based nanocomposite membrane containing finely dispersed MM-CNT with improved thermal stability to work as an electrolyte membrane at high temperature ($>100^\circ\text{C}$) PEM fuel cells.

2. Materials and methods

2.1. Chemicals required

Montmorillonite K10 (CEC = 80 mequiv./100 g), ferric nitrate nano hydrate (99.9% purity), sodium chloride (99% purity), 5 wt% Nafion solution, ethanol, dimethyl formamide (DMF) and dimethyl acetamide (DMA) used in this study were purchased from Sigma Aldrich and used as received.

2.2. Synthesis of montmorillonite supported iron catalysts

Na-montmorillonite was prepared by ion exchange of 10 g of montmorillonite with 1 M NaCl to ensure that all the exchangeable cations are only Na^+ . 20 and 25 wt% iron impregnated montmorillonite catalysts (MM 1 and MM 2 respectively) were prepared by dispersing Na-montmorillonite in a solution (5–8 ml) containing appropriate amount of ferric nitrate nano hydrate. The precursor was stirred vigorously for 3 h to ensure homogeneous mixing and then allowed to evaporate water slowly at 80°C in an air oven. Finally the catalysts were calcined at 450°C in air atmosphere to get iron oxide from their precursor.

2.3. Growth of carbon nanotubes

200 mg of catalyst (M_C) was taken in a quartz boat and placed in a quartz reactor which was kept in a horizontal tube furnace. Then the reactor was purged with nitrogen gas for about 20 min to remove any moisture present in the reactor. Later the furnace was heated at a rate of $15^\circ\text{C}/\text{min}$ to reach 850°C under the flow of nitrogen (60 ml/min) and hydrogen (60 ml/min). At 850°C pure hydrogen was passed into the reactor (1 h) to reduce iron oxide into iron nanoparticles. Then CNT growth was started by passing nitrogen (55 ml/min), hydrogen (55 ml/min) and acetylene (10 ml/min) over the freshly reduced catalyst for 1 h. After the completion of growth period the furnace was cooled to room temperature with nitrogen flow (60 ml/min). Finally the quartz boat containing montmorillonite-carbon nanotube (MM-CNT) hybrid was taken out, weighed and transferred to a plastic container. MM-CNTs obtained over MM 1 (20 wt% of Fe) and MM 2 (25 wt% of Fe) catalysts are represented as MM-CNT 1 and MM-CNT 2 respectively.

2.4. Fabrication of Nafion-MM-CNT nanocomposite membrane

Nafion based nanocomposite membrane containing MM-CNT nanofillers were prepared using solvent casting method [20].

Defined amount of MM-CNT 1 to attain 2 wt% filler content in the nanocomposite was dispersed in deionised water. Then a mixture containing 5 wt% Nafion solution, DMF, DMA and ethanol with a volume ratio of 4:1:1:4 was added to the aqueous dispersion of MM-CNT 1. The entire mixture was kept in ultrasonicator for 1 h at room temperature in the pulse mode to keep constant temperature. Later the mixture was stirred mechanically at 95°C until the solution concentration reaches the gelation point. Finally the gel obtained was casted in a glass plate and dried at 95°C in a hot air oven for 20 h and followed by annealing at 140°C for 24 h.

2.5. Characterisation of MM-CNT and Nafion-MM-CNT nanocomposite membrane

The growth features of carbon products and the dispersion of MM-CNT in the Nafion matrix were recorded using a SEM-JEOL 6460 LV, operating at 20 kV. The morphology, dimension and crystalline structure of the CNT obtained were investigated using TEM – JEOL 2000 EX, operating at 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera. The crystalline quality of CNTs was evaluated by measuring Raman scattering excited line at 514.5 nm of Ar^+ laser (Coherent Innova 70). The thermal decomposition pattern of Nafion solution, MM-CNT and nanocomposite membrane (2–3 mg of mass) was monitored in the temperature range between 25 and 800°C in a mixture of nitrogen and air atmosphere by Netzsch-STA 409 PC/PG thermogravimetry analyser (balance sensitivity: 0.1 μg).

3. Results and discussion

3.1. Yield evaluation

The yield of carbon nanotubes was calculated using the formula [21],

$$\text{carbon yield (\%)} = \left(\frac{m_{\text{tot}} - m_{\text{cat}}}{m_{\text{cat}}} \right) \times 100$$

where m_{cat} is the weight of the catalyst taken, m_{tot} is the weight of the hybrid materials (MM-CNT 1 and MM-CNT 2).

The carbon yield obtained over the catalysts MM 1 and MM 2 was 87.9% and 117% respectively, which clearly indicates the improved catalytic activity of the MM 2 catalyst because of the higher metal loading. The ratio of montmorillonite and CNT present in the resulting hybrid materials namely MM-CNT 1 and MM-CNT 2 is 1:0.87 and 1:1.17 respectively. The presence of CNT ratio 0.87 in MM-CNT 1 suggests that it is a good nanofiller (up to 2 wt%) for preparing the Nafion composite membrane without the risk of short circuiting by keeping the CNT content below the percolation threshold [17].

3.2. X-ray diffraction analysis

X-ray diffraction patterns of iron impregnated montmorillonite catalysts shown in Fig. 1 confirm the deposition of hematite ($2\theta = 33.1^\circ$) form of iron oxide over montmorillonite and the enhancement in the peak intensity is due to increased iron loading. The peaks identified in the diffraction pattern at 2θ 20° , 35° and 54° are indexed for the (1 1 0), (1 0 5) and (2 1 0) planes of montmorillonite respectively. Appearance of few additional diffraction lines is because of the presence of impurities such as muscovite and quartz in montmorillonite. The particle size of the iron oxide nanoparticles in MM 1 and MM 2 catalysts measured by Debye Scherer equation is 18 nm and 19 nm respectively. The characteristic peak of metallic iron particles appeared at 2θ 44.7° in the XRD pattern (Fig. 1) of the hybrid materials shows that iron oxide loaded over montmorillonite was reduced to metallic iron during reduction process. Another peak observed at 2θ 26.5° corresponds to

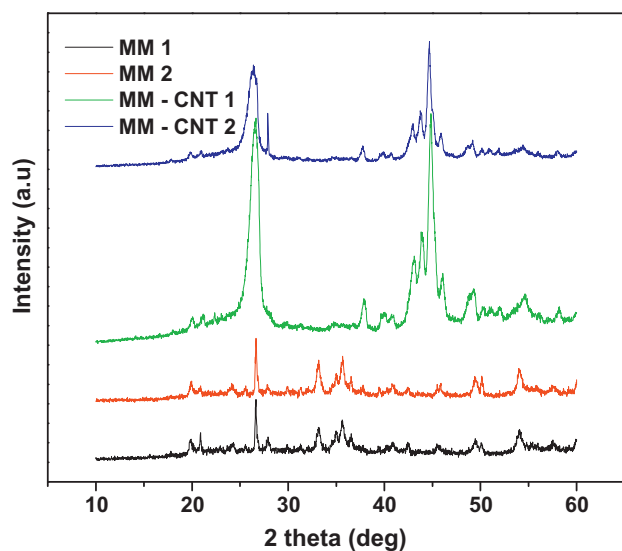


Fig. 1. X-ray diffraction patterns of the catalysts and hybrid materials.

the (002) planes of the graphitised multiwalled carbon nanotubes present in MM-CNT hybrid materials.

3.3. Morphological and crystalline analysis of nanofillers

High selectivity of carbon nanotubes was observed in the micrograph (Fig. 2) of MM-CNT 1 compared to MM-CNT 2 where the presence of little amount of graphitic structure was also seen. The improved selectivity over MM 1 is due to fine dispersion of the iron nanoparticles over montmorillonite. On the other hand MM 2 catalyst contains comparatively larger iron particles which tend to

deposit the carbon atoms as graphite rather than CNTs. The purity of CNTs is high without the presence of notable quantity of amorphous carbon. TEM images (Fig. 3) of MM-CNT 1 and MM-CNT 2 nano hybrid materials clearly show the formation of open ended multiwalled carbon nanotubes with good central channel. Open ended CNTs without iron particles at the tip confirm the root growth mechanism for the formation of CNT. The root growth is more preferred when CNT is used for polymer reinforcement applications because there is no need to open the end of the tube to remove any metal catalysts. The average outer diameter of the CNTs is 25 nm which depends on the size of the iron nanoparticles measured from corresponding X-ray diffraction pattern of the catalysts.

Raman spectra of the two different nanohybrids are shown in Fig. 4. G band at 1570 cm^{-1} aroused from the plane optical mode of the carbon nanotubes and the D band appeared at 1322 cm^{-1} is due to the presence of ill-organised graphites with lattice defects such as vacancies, pentagons, and heptagons. The I_D/I_G value derived from the quantitative measurement of the Raman spectra is the measure of the crystallinity of the CNTs formed. The I_D/I_G values calculated for MM-CNT 1 and MM-CNT 2 are 0.53 and 0.82 respectively, which indicates the significant growth of highly crystalline CNTs over montmorillonite compared to the previous literature reports [22]. The morphological analysis and crystalline assessment of the two nanofillers suggested that MM-CNT 1 would be better candidate to prepare Nafion based nanocomposite membrane.

3.4. Morphological and thermal behaviour of nanocomposite membrane

Achieving homogeneous dispersion of nanofillers in the Nafion matrix is very significant in making high performance composite membranes. The degree of dispersion of carbon nanotubes is studied from the SEM micrograph of Nafion-montmorillonite-carbon nanotube (Nafion-MM-CNT) nanocomposite membrane (Fig. 5). A

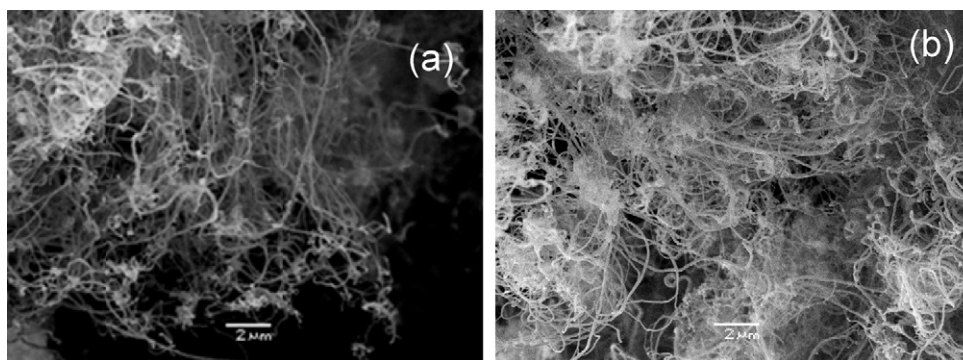


Fig. 2. SEM images of nanohybrid (a) MM-CNT 1 and (b) MM-CNT 2.

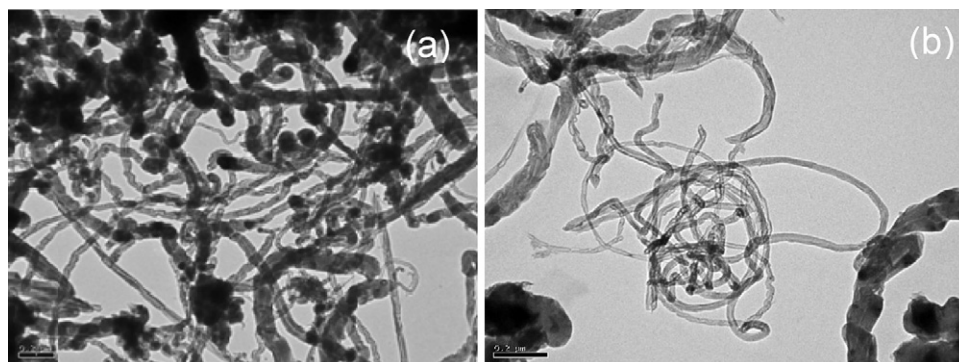


Fig. 3. TEM images of nanohybrid (a) MM-CNT 1 and (b) MM-CNT 2.

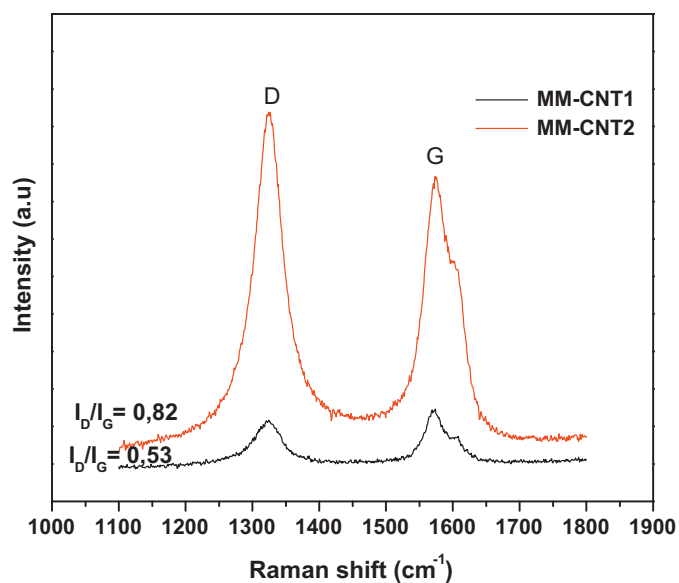


Fig. 4. Raman spectra of carbon products.

very fine dispersion of carbon nanotubes into Nafion matrix was observed because of the presence of CNTs in the clay platelets. The layered structure of montmorillonite favours the uniformity of polymer molecules over CNTs. The broken ends of the carbon nanotubes are observed from the uniformly distributed small bright dots and lines. The appearance of dense CNTs in some particular spots in the composite is due to the presence of CNTs over clay platelets. The presence of broken CNTs (without being expelled out of the matrix) in the composite membrane is another confirmation for the strong interaction of MM and CNT with Nafion. The corresponding EDS analysis of the selected area shows the presence of constituent elements of montmorillonite, CNTs and Nafion such as C, F, Al, Si and Fe, which confirms the homogeneous dispersion of montmorillonite and CNTs in the Nafion matrix.

The differential thermogravimetric (DTG) scans of Nafion solution, MM-CNT 1, Nafion-MM-CNT nanocomposite are shown in Fig. 6. The single narrow peak seen in the thermogram of MM-CNT 1 in the temperature range between 450 and 650 °C evidences the high crystallinity of the carbon nanotubes (Fig. 6b). The thermogram of Nafion contains three major weight losses because of the loss of boundary water molecules (which could not be completely removed at 100 °C) between 30 and 300 °C, occurrence of desulphonation process in the temperature range 380–430 °C and the decomposition of polytetrafluoroethylene (PTFE) backbone

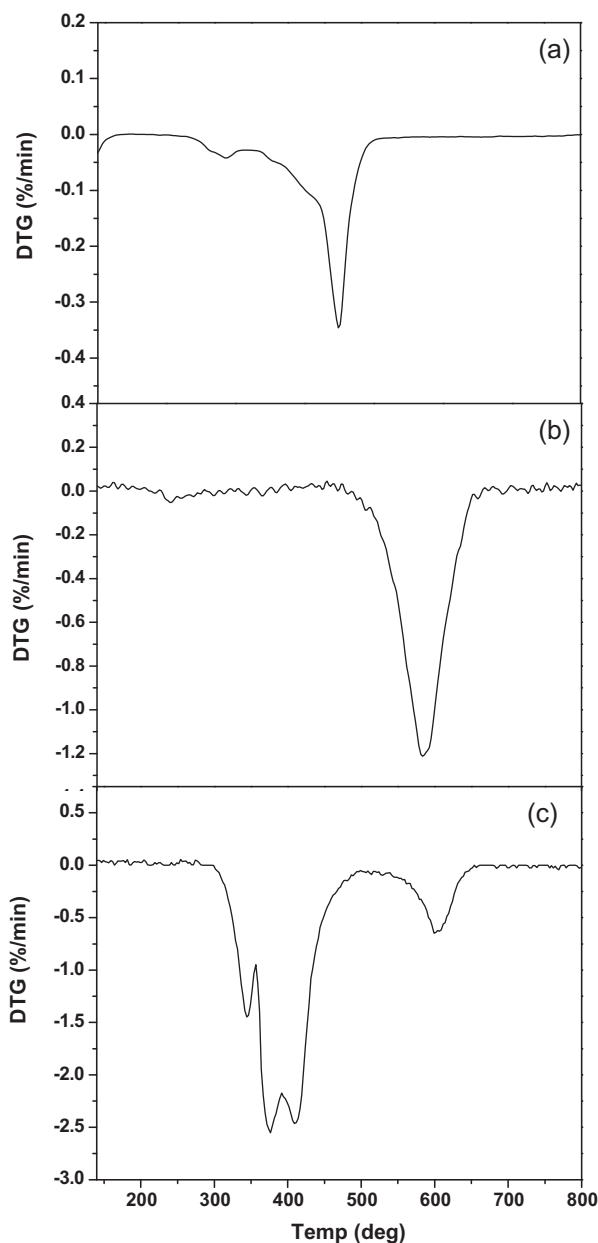


Fig. 6. DTG scan of (a) 5 wt% Nafion solution, (b) MM-CNT 1 and (c) Nafion-MM-CNT nanocomposite.

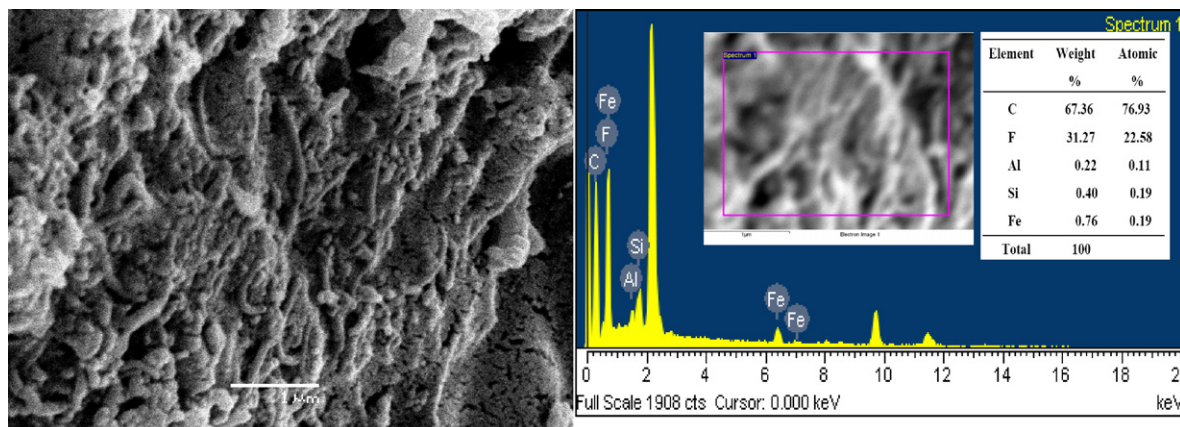


Fig. 5. SEM micrograph of Nafion-MM-CNT nanocomposite (left) and the corresponding EDS analysis (right).

between 430 and 550 °C [23]. From the figure it seems that the degradation of Nafion-MM-CNT nanocomposite also follows the degradation pattern of the pure Nafion as reported by Cele et al. [23]. But the increase in the temperature corresponding to the onset thermal degradation (up to 480 °C) evidenced the improved thermal stability of the Nafion-MM-CNT composite. The two separate humps between 380 and 480 °C are attributed to the decomposition of sulphonic acid which has an interfacial interaction with the hydroxyl group of the montmorillonite. The homogeneous dispersion of CNTs rooted on montmorillonite enhances the thermal stability because of the improvement in the activation energy for degradation. The presence of thermally more stable CNTs favours the extra stability (up to 630 °C) of the PTFE backbone in the nanocomposite.

The improved thermal stability of the composite membrane is due to the homogeneous dispersion of the 3D nanostructured CNT-clay nanohybrid (which consists of CNT (1D) and MM (2D)) in the Nafion matrix and the strong interaction between them. The synergistic effect observed is due to the fact that attached growth of CNTs on the clay delaminates the platelets and also prevents the CNTs from being entangled and aggregated. The nanotubes also serve as hydrophobic tails for the dispersion of the hydrophilic clay platelets in the polymeric matrix [24]. The interaction of the polymer chains with the hybrid filler seems to be much stronger compared to smooth CNTs alone or clay platelets alone, because of the fact that the polymer chains are entangled and wrapped around the 3D nanostructured filler.

4. Conclusions

Fabrication of defects free Nafion based nanocomposite membrane is essential in developing high performance PEM fuel cells. In this research work we made a successful attempt to accomplish the combined effect of clay and carbon nanotubes in the Nafion matrix to overcome its limitations. Carbon nanotubes rooted montmorillonite was successfully synthesised by cost effective catalytic chemical vapour deposition method. The clay was exfoliated to well-separated nanoplatelets by intercalation with iron (oxide) followed by the growth of CNTs. Highly selective defects free crystalline CNTs ($I_D/I_G = 0.53$) were obtained. TEM micrograph confirms the formation of open ended CNTs (from root growth mechanism), which are very suitable for polymer reinforcing applications. MM-CNT containing Nafion based nanocomposite membrane was fabricated by solution casting method. The homogeneous dispersion of the CNTs in the Nafion matrix was achieved in the presence of layered structure of montmorillonite. The combined effect of montmorillonite and CNTs leads to the improved thermal stability of the nanocomposite membrane. The observed results suggest

that this nanocomposite membrane would significantly enhance the performance of PEM fuel cells. This approach greatly simplifies the overall process for making high-performance nanocomposites membranes to be used in PEM fuel cells. Further studies on the mechanical strength and methanol permeability of the nanocomposite membrane are in progress.

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