Interactions between Nafion resin and protonated dodecylamine modified montmorillonite: A solid state NMR study

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Abstract

A series of nanocomposites have been prepared from perfluorosulfonylfluoride copolymer resin (Nafion) and layered montmorillonite (MMT) modified with protonated dodecylamine by conventional sol–gel intercalation. The structure of these nanocomposite materials have been characterized using FT-IR, elemental analysis, XRD and solid state NMR techniques, including 19F magic-angle spinning (MAS) NMR, 19F NMR relaxation time measurements, 29Si MAS, 1H MAS, 1H-13C cross-polarization magic-angle spinning (CPMAS), and 1H-13C heteronuclear correlation (HETCOR) 2D NMR. The results showed that thermal stability of Nafion was improved moderately by the addition of dodecylamine modified MMT without intercalation. FT-IR and 29Si MAS NMR results indicated that dodecylamine modification did not result in obvious changes in the MMT lattice structure. The XRD results showed that the protonated dodecylamine has been embedded and intercalated into the MMT interlayers, whereas Nafion was not. Elemental analysis results also suggested that some dodecylamine was adsorbed on the surface of MMT. 1H-13C HETCOR 2D NMR experiment clearly indicated that strong electrostatic interactions were present between the NH₃⁺ group of dodecylamine and the fluorine-containing groups (–CF₃, –OFCF₂, and –SCF₂) of Nafion resin. Such electrostatic interactions are probably the major contributors for the improved thermal stability of the resultant composite materials.

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1. Introduction

Direct methanol fuel cell (DMFC) is one of the most promising systems for widespread applications in portable power sources, electrical vehicles, and transportation devices where both high efficiency and light weight are vitally important [1]. The high temperature proton-exchange membrane (PEM) is essential for the life span of those fuel cells. Nafion resin (Fig. 1) represents one of the most thermally stable membranes and is by far the most extensively studied proton electrolyte membrane [2–6], whose mechanism of conduction is due to the higher proton ion transportation [7–9]. In practice, however, normal Nafion materials are not applicable for DMFC due to two major limitations, namely, high rate of methanol permeation [10,11] and poor mechanical stability at temperature above 100°C. Nafion also suffers from the fact that conductivity is present only when soaked into the water, resulting in an operating temperature of 80°C [12,13]. Therefore, there are still some needs for further development in the membrane materials with high thermal, mechanical and chemical stability.

In order to develop the higher temperature electrolyte materials, many attempts have, so far, been made by modifying the Nafion membrane with various nonconductive inorganic materials such as silica, titania, zirconia, laponite, and montmorillonite (MMT) [14–24]. When applied to DMFCs, these composite materials containing inorganic moieties also reduced the methanol crossover. Amongst these inorganic materials, natural MMT has shown some promises since it is an abundant and inexpensive layered silicate with large surface areas, which has already been widely used as raw material for nanocomposites [25,26]. Previous work has already shown that introduction of MMT or metal oxide into Nafion has improved the membrane thermal stability moderately, resulting in a material which was stable at temperature as high as 100°C [13,27,28].
However, little information is available on what interactions were responsible for such thermal stability improvement. In addition, there are few reports dealing with the molecular structure of these composite materials, the interactions between the inorganic and organic species at the molecular level and structure-property relationships, which will undoubtedly be useful for future development of materials. For the organic modified MMT (m-MMT), the organic modifiers may be present in two states, intercalated into the MMT layers and adsorbed on the MMT surface [29,30] depending upon the amounts of organic modifiers with respect to the cation exchange capacity (CEC) of MMT. Such surface absorption is often strong enough to prevent from being washed out during m-MMT preparation [29,30]. However, some questions remain unanswered, such as: 'where are there any effects of the surface adsorbed modifiers on the composites,' 'are there any interactions between the surface adsorbed organic modifier and other species in the case of m-MMT/polymer systems,' 'what is the mode of action for these interactions,' 'what is the importance of these interactions to the macroscopic properties.' In order to answer some of these questions in the present work, a series of nanocomposite materials were prepared containing various amounts of organic modified MMT by conventional sol–gel intercalation method. The structure, dynamics and interactions in these materials were studied using FT-IR, XRD, and elemental analysis as well as a catalogue of solid state NMR techniques. The results will be interpreted with the aims of understanding the interactions between resins and m-MMT; and the implications in the alterations to the thermal stability of the resultant membrane.

2. Experimental

2.1. Preparation of nanocomposite materials

2.1.1. Functionalization of MMT

Raw MMT (supplied from Wuhan University of Technology, China, cation exchange capacity CEC, 0.96 mmol/g) was treated with a solution of 20% NaOH/methanol (2:1 v/v) at 90°C for 2 h followed with deionized water washing till no rufous Fe(OH)₃ precipitate was observed with addition of some drops of 20% NaOH. To convert Na⁺-MMT into H⁺-MMT, the material was immersed in 1 M H₂SO₄ solution for 3 h at 90°C and rinsed repeatedly with sufficient deionized water. Dodecylamine modified montmorillonite (m-MMT) was synthesized from dodecylamine (purchased from Sigma–Aldrich, Inc.) by a cation exchange reaction. Briefly, 9 g dodecylamine was dissolved in 100 ml HCl solution (0.05 M) at 80°C followed with addition of the MMT suspension (20 g treated MMT in 400 ml deionized water). The mixture was then stirred at 80°C for 2 h with magnetic stirrer. The functionalized MMT (m-MMT) was recovered by filtration and washed with sufficient deionized water repeatedly for at least 3 times. The MMT and m-MMT were dried in an oven for 24 h and sieved through a sieve (<330 mesh) to remove the coarse particles.

2.1.2. Fabrications of composite materials

The composite materials were prepared using the following sol–gel procedure. A desired amount of m-MMT was added to a Nafion solution (DuPont, 5 wt%), then stirred mechanically for 8 h followed with ultrasonication degassing so as to make the contents of m-MMT in the mixture 3, 5, 8, and 10 wt% (based on Nafion resin), respectively. The prepared mixture was then slowly poured into a petridish to form a composite membrane with thickness of ca. 0.1 mm. The filled glass dish was placed in a vacuum oven and dried by slowly increasing the temperature from 80 to 130°C to prevent the formation of crevices in the composite membrane. The residual solvent in the composite membrane was fully removed by evacuation at 130°C for 12 h. The composite materials were finally obtained by annealing the membranes at temperature higher than the glass transition temperature of Nafion resin (~230°C). The prepared membrane samples were used to do conductivity, TGA, FTIR, elemental analysis and XRD measurements without further treatment. For NMR measurements, the m-MMT and nanocomposite materials were vacuum-dried (10⁻¹ Pa) by heating samples up to 80°C with a rate of 1 °C min⁻¹ and then kept at that temperature for 12 h to remove water.

2.2. Characterization of the prepared materials

2.2.1. Thermal stability analysis of composite materials

The composite materials with various m-MMT contents were analyzed under nitrogen gas with TGA/DSC (SETARAM TG-DSC 92) by heating the materials from 30 to 600°C with a heating rate of 10°C/min. The percentage weight loss for the resin was calculated to be an indicator of the thermal stability.

2.2.2. Proton conductivity measurements

The proton conductivity of the nanocomposite materials was measured by using impedance analyzer at room temperature. The impedance measurements were performed on a frequency-response analyzer (Solatron SI 1260, impedance/gain-phase analyzer) with an alternating current. The frequency range was 0.01–10⁶ Hz and the current amplitude was 0.01 mA. The composite membrane was fixed in a four-point probe cell consisting of two platinum wire outer current-carrying electrodes and two platinum wire inner potential-sensing electrodes. The structure of the cell was fabricated from PTFE material. The conductivities of the materials were calculated according to \( Q = \alpha/(R \ast a \ast b \ast c) \), where \( Q \) and \( R \) denote the ionic conductivity and the resistance of the membrane, respectively, \( a, b, \) and \( c \) denote the length, width and thickness of the membrane respectively. The conductivities of the materials were measured in wet and dry environment at room temperature. The wet membrane was obtained by immersing the dry one in deionized water sufficiently for 12 h. Water on the surface was removed for the
measurement of the proton conductivity. The water content was 13 wt% for neat Nafion and less than 27 wt% for composite membranes.

2.2.3. Elemental analysis

Elemental analysis of m-MMT was carried out using an elemental analyzer RARIO EL III. A custom built potentiostat connected to a computer with an AD/DA converter was used to record cyclic voltammograms (CVs).

2.2.4. FT-IR spectroscopy

The FT-IR experiments of MMT and dodecylamine modified MMT (m-MMT) were performed on a FT-IR spectrometer (MAGNA 560, Nicolet Co.) and the spectra were recorded in the wave number range from 400 to 4000 cm\(^{-1}\) with the KBr pellet method.

2.2.5. X-ray diffraction

The XRD patterns of the montmorillonite crystal were recorded before and after the intercalation with organic Nafion copolymer resin on a MAC Science Co. M18XHF diffractometer equipped with a liquid nitrogen-cooled germanium solid-state detector. CuK\(\alpha\) radiation (40 kV, 200 mA) was used as an X-ray source to measure the change in d-spacing of the layered silicate and the composite materials. The 2\(\theta\)-scanning rate was 2° min\(^{-1}\). The repeat distance in the silicate was calculated using Bragg’s law, \(d = \lambda / 2 \sin \theta_{\text{max}} \), where \(\theta_{\text{max}}\) is the position of the (001) peak in the XRD pattern.

2.2.6. Solid state NMR spectroscopy

All NMR experiments were performed at 25 °C. The \(^{19}\)F NMR experiments were carried out on a Varian InfinityPlus-300 spectrometer equipped with a 2.5 mm double-resonance magic-angle spinning probe, operating at 376.45 MHz for \(^{19}\)F. The powder samples were packed into a zirconia rotor and spun at 25 kHz (±1 Hz). The \(^{19}\)F spin-lattice relaxation times in the laboratory (\(T_1\)) and rotating frames (\(T_{1\rho}\)) were measured using standard inversion-recovery and spin-locking pulse sequences respectively to probe the molecular dynamics of the Nafion resin. The \(^1\)H MAS, \(^{1}\)H-\(^{13}\)C CPMAS, and \(^1\)H-\(^{13}\)C HETCOR 2D NMR spectra were recorded on a Varian InfinityPlus-300 spectrometer equipped with a 4 mm double-resonance magic-angle spinning probe head, operating at 299.98 MHz for \(^1\)H and 75.12 MHz for \(^{13}\)C, respectively. For CPMAS and HETCOR NMR experiments, contact time was 2 ms and a proton decoupling field strength of 70 kHz was used during the acquisition time. \(^{29}\)Si MAS NMR spectroscopy was recorded on a Varian InfinityPlus-300 spectrometer equipped with a 7.5 mm magic-angle spinning probe head with a sample spinning rate of 5 kHz (±1 Hz). The chemical shifts were referenced to tetrathylsilane (TMS) for \(^1\)H and \(^{29}\)Si (0 ppm for \(^1\)H, -9.8 ppm for \(^{29}\)Si), to hexamethyldisilazane (HMDS) for \(^{13}\)C (17.35 ppm for CH\(_3\)), to CF\(_3\)COOD for \(^{19}\)F (−78.5 ppm), respectively. The recycle delay was 5 s for \(^1\)H MAS, \(^1\)H-\(^{13}\)C CPMAS, and \(^1\)H-\(^{13}\)C HETCOR 2D NMR, 3 s for \(^{19}\)F MAS and 100 s for \(^{29}\)Si single pulse experiments. The 90º pulse lengths for \(^1\)H, \(^{19}\)F, and \(^{29}\)Si were measured to be 4.3, 3.7, and 4.8 µs, respectively.

![Fig. 2. Thermal stability of Nafion/layered silicate composite materials with various content of m-MMT. Weight loss for the Nafion resin as a function of temperature.](image)

3. Results and discussion

3.1. Thermal stability of composite materials

The thermal stability of Nafion resin and the nanocomposite materials with dodecylamine modified MMT (m-MMT) were investigated by TGA and the weight loss of Nafion resin were used as an indicator for its thermal stability. The results showed that the resin itself lost about 5 wt% weight between 25–125 °C whereas the m-MMT-resin composites showed about 3 wt% weight loss of weight. Therefore the weight loss for them was probably due to loss of absorbed water. Between 125 and 250 °C, resin showed weight loss of 3 wt% whereas resin containing 10 wt% m-MMT showed 1 wt% weight loss (see Fig. 2, insert). This was probably due to the loss of SO\(_2\) and CO\(_2\) gases [27]. In comparison, about 7–20 wt% loss was observed for m-MMT-resin composites between 280 and 380 °C attributable to the further loss of SO\(_2\), CO\(_2\) and the release of SF\(_4\), CO, and CF [31]. Our observed weight loss associated with the Nafion backbone CF and CF\(_2\) is also moderate compared with the high temperature (450–560 °C) treatment where as much as 92 wt% of the material volatilized. These suggested that all the Nafion resin/m-MMT nanocomposite materials had some moderate thermal stability improvement compared with the copolymer resin itself (Fig. 2) and the thermal stability of the composites appeared to be positively correlated with the m-MMT contents.

3.2. Proton conductivity

The proton conductivities of Nafion resin/m-MMT nanocomposite materials were analyzed at ambient using impedance analyzer in the dry and wet states, respectively. The results (Table 1) showed that the pure Nafion membrane had higher proton conductivities than the composite materials. Proton conductivities also showed greater decrease as a function of the m-MMT contents in the dry state than that in the fully hydrated nanocomposite materials. Nevertheless, the overall proton conductivity
decrease for the composite materials is moderate (4–10%). It is, therefore, anticipated that the composite materials are still suitable as electrolyte membrane for DMFCs.

3.3. Elemental analysis

The results of elemental analysis showed that in the organic modified MMT the dodecylamine concentration was about 1.76 mmol/g, being much higher than the cation exchange capacity of MMT (0.96 mmol/g). Therefore, it is conceivable that besides the intercalated surfactant (shown by XRD data below), there is still some surfactants deposited on the outside of MMT. Such deposits may be the result of surface absorption of amine ions on the clay which can not be washed out repeatedly with deionized water (AgNO3 test).

3.4. FT-IR spectroscopy

FT-IR spectra (data not shown) of the MMT and m-MMT showed absorption bands (3624, 3421–3447, 1620–1640 cm⁻¹) attributed to hydroxyl stretching of the silicate lattice, water in the interlays and hydroxyl bending of adsorbed water, respectively, suggesting the presence of some adventitious adsorbed water. The broad bands at 1034–1036 cm⁻¹ and a weak band at 793 cm⁻¹ can be assigned to the stretching of Si–O–Si and Si–O–Al in the MMT lattice, respectively. The bands at 520 and 466 cm⁻¹ correspond to bending of Si–O–Si and Si–O–Al, respectively. Two sharp bands at 2922 and 2852 cm⁻¹ were observed in the FT-IR spectrum of the dodecylamine modified MMT, corresponding to the symmetrical and asymmetrical stretching of the –CH₂ group in dodecylamine, respectively. The band at 1469 cm⁻¹ is assigned to the –CH₂ bending of the organic modifier. FT-IR spectra showed that upon dodecylamine modification there were no outstanding changes in the lattice structure of MMT. This is consistent with previous observations in the similar situation [10] and observations from ²⁹Si NMR results which will be further discussed in Section 3.5.

3.5. X-ray diffraction

Normally, the persuasive evidence for the intercalation of a modifier into the interlayer of MMT can be obtained from XRD patterns of the nanocomposites. By monitoring the position, shape and intensity of diffraction peaks, the embedded or intercalated structure of the nanocomposites can be identified. For intercalated nanocomposites, the finite layer expansion associated with the modifier intercalation usually results in appearance of a new basal reflection corresponding to the larger gallery height. Fig. 3 shows the XRD patterns of the purified MMT (Fig. 3a), dodecylamine modified MMT (m-MMT) (Fig. 3b) and the corresponding nanocomposites containing various contents of the m-MMT (Figs. 3c–3f) in the 2θ range 1°–50°. The d-spacing values of the MMT, m-MMT and the composites are calculated and summarized in Table 2. The average interlayer spacing for the MMT powder obtained from XRD measurement is 11.39 Å (2θ = 6.33°). Dodecylamine modification resulted in an increase of about 4.80 Å in the interlayer spacing, indicating the formation of intercalated structure. Previous report [32] showed that when dodecyldimethylammonium cation was intercalated into MMT as a lateral monolayer, the quaternary ammonium cation (–N(CH₃)₄⁺) head group resulted in an increase of about 5.10 Å in the interlayer spacing. The head group (ammonium cation) in our system is about two N–H bonds in length, thus about 2 Å, which is much smaller than that of quaternary trimethylammonium cation. It is therefore reasonable to assume that the organic modifier (dodecylamine) may adopt a bi-layer arrangement in the gallery of MMT [32].

When Nafion resin was introduced into the m-MMT, the basal spacing values only increased moderately (see Table 2) compared to that of m-MMT, even though the d-spacing of m-MMT increases with the increasing of the m-MMT contents. Even the greatest d-spacing increase (3.45 Å) following Nafion resin introduction is still much smaller than what literature reported intercalated systems (15.98 Å) [10]. This suggests that in our cases the side chain groups of Nafion resin is probably not intercalated into the interlayer of m-MMT; the Nafion resin is probably located outside of the gallery of m-MMT. However, the thermal stability improvement for these composites can still

| Table 1 | Proton conductivity of pure Nafion resin and Nafion/layered silicate composite materials with 3 wt% m-MMT, 8 wt% m-MMT in the dry and wet state at room temperature |
| Membrane | a (cm) | b (cm) | c (cm) | R (Ω) | Q (Ω⁻¹·cm⁻¹) |
| Nafion resin | Dry | 6 | 1 | 30 | 49.1 | 0.00407 |
| | Wet | 6.6 | 1.2 | 37 | 16.8 | 0.00885 |
| Nafion/3 wt% m-MMT | Dry | 6 | 1 | 115 | 21.3 | 0.00245 |
| | Wet | 6.8 | 1.3 | 135 | 4.55 | 0.00852 |
| Nafion/8 wt% m-MMT | Dry | 5 | 1 | 80 | 132 | 0.00147 |
| | Wet | 5.7 | 1.3 | 95 | 5.79 | 0.00797 |

Fig. 3. XRD patterns of MMT (a), m-MMT (b) and Nafion/layered silicate composite materials containing various contents of m-MMT (c: 3 wt% m-MMT; d: 5 wt% m-MMT; e: 8 wt% m-MMT; f: 10 wt% m-MMT).


41
be attributed to the interactions between m-MMT and resin, the details of which are expected to be accessible with solid state NMR techniques.

3.6. Solid state NMR spectroscopy

$^{29}$Si MAS NMR spectra (data not shown) of MMT, m-MMT and nanocomposites containing various contents of m-MMT showed that three signals are observable at about −92, −102, and −111 ppm, corresponding to Q$^2$ (Si(OSi)$_2$(OH)$_2$), Q$^3$ ((Si–O–)$_2$Si(–O–Si)(–OH)) and Q$^4$ ((Si–O–)$_3$Si(–O–Si)) sites, respectively. This is in good agreement with the previously published observations for MMT [28]. However, the peaks (−30 to −60 ppm) due to the so-called ‘T’ sites [33,34] are not observed in the $^{29}$Si NMR spectra. This indicates that the lattice structure of MMT was not drastically changed by the organic modifier and Nafion resin, being consistent with our FT-IR results discussed above.

Fig. 4 shows the $^{19}$F MAS NMR spectra of Nafion resin alone and the nanocomposite materials containing various contents of m-MMT. $^{19}$F resonances are observed at about −146, −139, −122, −117, and −80 ppm which are assigned to side chain CF, backbone CF, (CF$_2$)$_m$, CF$_2$ attached to SO$_2$ group and CF$_2$/OCF$_2$ groups respectively according to Refs. [35,36]. The $^{19}$F line widths of −CF$_3$, −OCF$_2$, and −SCF$_2$ in the side chain of Nafion resin increase with the increase of m-MMT contents, as depicted in Table 4, whereas this trend is not observed in the other $^{19}$F sites resonating at −122, −138, and −144 ppm. This indicates that side chain groups of Nafion resin may be involved in the interactions with m-MMT, limiting the motion of these groups. Although the nature of interactions requires further evidence to be ascertained, the SO$_3^−$ group of resin and NH$_3^+$ group of dodecylamine are probably the responsible groups. $^{19}$F relaxation time measurements (Tables 3 and 4) showed that the $^{19}$F $T_1$ (s) and $T_{1\rho}$ (ms) values for −CF$_3$, −OCF$_2$, and −SCF$_2$ groups increased clearly with the rise of m-MMT concentration whereas the $^{19}$F $T_1$ (s) and $T_{1\rho}$ (ms) values for the other groups remained almost unchanged. This indicates again that the molecular motions of the −CF$_3$, −OCF$_2$, and −SCF$_2$ groups are considerably restricted, probably due to the interactions between the −CF$_3$, −OCF$_2$, and −SCF$_2$ of Nafion resin and m-MMT. Since the lattice structure of MMT was not changed by the organic modifier and Nafion resin, it can be concluded that the Nafion resin may not strongly interact with MMT. However, the interactions between the Nafion resin and the organic modifier (protonated dodecylamine) cannot be ruled out and ought to be accessible by NMR.

$^{1}$H MAS NMR spectra of vacuum-dried MMT sample (data not shown) showed only one signal at about 1.4 ppm corresponding to OH groups of MMT [37] and the Nafion spectrum showed a proton signal at 9.6 ppm assigned to the SO$_3$H group [38]. No $^1$H signals were observed for the sodium hydroxide treated Nafion, indicating no water present. $^1$H MAS NMR spectra of m-MMT and Nafion/8 wt% m-MMT showed two signals at 1.4 and 6.5 ppm. The high field signal (1.4 ppm) can be assigned to the OH group of MMT and alkyl chain protons whilst the signal at δ = 6.5 can be assigned to the NH$_3^+$ group of the protonated dodecylamine. The areas were about 10:1 for the peaks at δ = 1.4 and 6.5. Taking the number of OH groups of MMT into consideration, such area ratio was about 8:1, being similar to the proton number ratio between alkyl and NH$_3^+$ group. This implies that there was no water present in the samples. The $^1$H-$^{13}$C CP MAS NMR spectra (Fig. 5) of m-MMT and the nanocomposites containing different contents of m-MMT (3, 5, and 8 wt%) showed $^{13}$C resonances at 16, 22, and 33 ppm corresponding to −CH$_3$, (−CH$_2$)$_n$, and −CH$_2$NH$_3^+$ groups, respectively. Two extra $^{13}$C signals at 119.4 and 113.5 ppm in the $^{13}$C CP MAS NMR spectra (Figs. 5b–5d) of the nanocomposites are assignable to the −CF$_3$, −OCF$_2$, and −SCF$_2$ groups of copolymer resin, respectively [35,36]. The appearance of the two resin signals suggests that there are some dipolar interactions between the organic modifier and Nafion resin, leading to the efficient $^1$H-$^{13}$C cross polarization. In addition, three $^{13}$C peaks of dodecylamine at 15, 22, and 30 ppm in m-MMT spectrum (Figs. 5b–5d) were shifted to higher field compared with those of dodecylamine itself (Fig. 5a), which probably results from the interactions be-

<table>
<thead>
<tr>
<th>Samples</th>
<th>Inter-layer distance</th>
<th>Δ (Å)</th>
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<tr>
<td>MMT</td>
<td>11.39</td>
<td>0$^a$</td>
</tr>
<tr>
<td>m-MMT</td>
<td>16.19</td>
<td>4.80$^b$</td>
</tr>
<tr>
<td>Nafion resin/3 wt% m-MMT</td>
<td>16.49</td>
<td>0.30$^b$</td>
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<tr>
<td>Nafion resin/5 wt% m-MMT</td>
<td>17.06</td>
<td>0.87$^b$</td>
</tr>
<tr>
<td>Nafion resin/8 wt% m-MMT</td>
<td>18.72</td>
<td>1.53$^b$</td>
</tr>
<tr>
<td>Nafion resin/10 wt% m-MMT</td>
<td>19.64</td>
<td>3.45$^b$</td>
</tr>
</tbody>
</table>

$^a$ Difference from MMT; $^b$ Difference from m-MMT.
Table 3

<table>
<thead>
<tr>
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<th>19F (T_1) (s)</th>
<th>19F (T_1\rho) (ms)</th>
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<tr>
<td>Nafion resin</td>
<td>0.65</td>
<td>2.92</td>
</tr>
<tr>
<td>Nafion resin/3 wt% m-MMT</td>
<td>0.73</td>
<td>3.08</td>
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<tr>
<td>Nafion resin/5 wt% m-MMT</td>
<td>0.82</td>
<td>3.22</td>
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<td>Nafion resin/8 wt% m-MMT</td>
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<td>3.43</td>
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<tr>
<td>Nafion resin/10 wt% m-MMT</td>
<td>0.93</td>
<td>3.50</td>
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\(a\) The fitted error was within 5%.

Table 4

<table>
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<th>19F line width (kHz)</th>
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<tr>
<td>CF(_3) OCF(_2) SCF(_2) (CF(_2))(_n) CF (B) CF (S)</td>
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<tr>
<td>Nafion resin</td>
<td>0.48</td>
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<tr>
<td>Nafion resin/3 wt% m-MMT</td>
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<td>Nafion resin/5 wt% m-MMT</td>
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<tr>
<td>Nafion resin/8 wt% m-MMT</td>
<td>0.61</td>
</tr>
<tr>
<td>Nafion resin/10 wt% m-MMT</td>
<td>0.64</td>
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Fig. 5. \(^{1}H\)-\(^{13}C\) CPMAS NMR spectra of m-MMT (a) and Nafion/layered silicate composite materials containing various contents of m-MMT.

Fig. 6 shows the \(^{1}H\)-\(^{13}C\) HETCOR 2D NMR spectrum of Nafion/layered silicate composite material containing 8 wt% m-MMT.

4. Conclusion

When dodecylamine was used to modify MMT, it will be readily intercalated into the layered silicate forming a bilayer arrangement. Elemental analysis suggested considerable part of surfactants was adsorbed on the surface of MMT. FT-IR and \(^{29}\)Si MAS NMR results showed no significant alteration to the lattice structure of m-MMT and addition of the organically modified MMT led to moderate improvement of the thermal stability of Nafion resin though the resin was not intercalated into the m-MMT. \(^{1}H\)-\(^{13}C\) HETCOR 2D NMR experimental results, combined with XRD and element analysis, indicated strong interactions between \(NH_3^+\) group of surface absorption
of dodecylamine and the SO$_3^-$ group of the resin side chain. It is concluded that interactions between the resin and the surface absorbed organic modifier probably have some contributions to the resin thermal stability enhancement resulting from addition of m-MMT.

Acknowledgments

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