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Nano-composite of Phosphoric Acid Derivative of Fullerene with SiO$_2$ and its Proton Conductivity

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The nano-composite of the phosphoric acid derivative of fullerene ([PO(OH)$_2$]$_3$CC$_{60}$) with SiO$_2$ was synthesized using the in-situ reaction from [PO(OH)$_2$]$_3$CC$_{60}$ with tetraethoxysilane (TEOS). The nano-composite was characterized using FT-IR measurements, and its morphology was observed using SEM. The humidity dependence of their proton conductivity for both [PO(OH)$_2$]$_3$CC$_{60}$ and its nano-composite was investigated. The proton conductivity of the nano-composite is increased more than one order of magnitude higher than that of [PO(OH)$_2$]$_3$CC$_{60}$ under low relative humidity. This is probably because the more proton conductive sites are generated by SiO$_2$. However its proton conductivity is lower in the humidity range above 60%, probably because the number of the highly dissociative protons from phosphoric acid is decreased after being combined with silica.

Key Words : Proton Conductor, Fullerene Derivative, Nano Composite, Fuel Cell

1 Introduction

Due to the potential applications for fuel cells, chemical sensors and batteries etc, proton conductive materials are attracting increasing interest. Many proton conductive materials such as Nafion,$^{1,3}$ 12-phosphotungstic acid,$^{4}$ zirconium oxide hydrate,$^{5,6}$ and tungsten oxide hydrate$^{7}$ have been extensively studied and reported. Unfortunately most proton conductors need high relative humidity (R.H.) to have high proton conductivity.

Recently, Hinokuma and Atn$^5$ had made a significant discovery that polyhydroxyfullerene (fullerol) C$_{60}$(OH)$_2$ is able to conduct protons. The proton conduction mechanism of this material is thought to be proton hopping through the oxygen sites on fullerene cages. The strong electrophilic property of fullerene allows protons to be easily dissociated. Proton conductivity is enhanced to about 10$^4$ S cm$^{-1}$ by introducing more acidic functional groups.$^9$ This discovery explored a new family of proton conductors based on fullerene.

In 2002, we reported another one kind of fullerene derivative named the phosphoric acid derivative of fullerene (PADF),$^{10}$ which shows strong humidity dependence. It was thought to be due to the difference in the number of functional groups on the fullerene cage. In addition PADF is easy to be dissolved into water. This is disadvantageous for the application especially to fuel cells.

Producing a nano-composite with SiO$_2$ is one of the methods to solve this disadvantage. Here are the examples of the research works on this material.

A research group headed by Honma at AIST of Japan has been working on silica based nano-composites composed with some water soluble inorganic proton conductors such as mono-dodecylphosphate, and 12-phosphotungstic acid using sol-gel processes.$^{11-13}$ The group focused on the application for the intermediate temperature fuel cell. Nagai et al.$^{14,15}$ contributed a number of papers on the nano-composite of silicon dioxide doped with silicotungstic acid or silicophosphate-HClO$_4$ gel. There is one more research group in the University of Tokyo$^{10}$ reported a composite of CsH$_2$PO$_4$ with silica. Matsuda et al.$^{17,30}$ produced a phosphosilicate gel from the tetraethoxysilane (TEOS) and H$_2$PO$_4$, which shows high proton conductivity of 1.5 × 10$^{-2}$ S cm$^{-1}$ at 130°C and 0.7% R.H.. In their reports, they presented the evidence of condensed phosphoric acid with a bridging oxygen of Si-O-P using $^{31}$P MAS-NMR.

We report here the first fabrication of a nano-composite of PADF with silicon dioxide. The characterization of this material, and its humidity dependence of proton conductivity are reported as well.

2 Experimental

2.1 Material preparation and characterization

The method of synthesizing methano [60] fullerene diphosphonate is the same as previously reported,$^{10}$ and is shown in Scheme 1.

After dissolving 1g (1.39 mmole) of C$_{60}$ in 500 ml dehydrated toluene, 352 mg of I$_2$ (1.39 mmole) and 5g of NaI (after being washed twice in dehydrated toluene) were added to the solution. Then 337 µl (1.39 mmole) of tetaethyl methylene diphosphonate was added while stirring. It was reacted for 24 hours under Ar gas at room temperature. The solution was filtered, and the precipitate was washed with CHCl$_3$. After the solvents were evaporated using a rotary evaporator, and washed with hexane, alcohol and toluene, the dark brown powder was obtained. It was then dried in a 50°C oven for two days to obtain the tetaethyl methano [60] fullerene diphosphonate ([PO(OC$_2$H$_5$)$_3$]$_2$CC$_{60}$) with a yield of 60%.

The hydrolysis process of ([PO(OH)$_2$]$_3$CC$_{60}$) to PADF, [PO(OH)$_2$]$_3$CC$_{60}$, was carried out in NaOH solution. After 0.5g of ([PO(OH)$_2$]$_3$CC$_{60}$) was added to 100 ml of
Scheme 1 Synthesis procedure for phosphoric acid derivative of fullerene.

1N NaOH solution, it was stirred in a Teflon® beaker at 50°C for 3 days. The suspension then turned into a dark brown solution. It was then ion-exchanged to give a strong acidic solution. This was dried using a rotary evaporator, and then dried under vacuum at 50°C for two days. The PADF, a brown powder, was obtained.

The in-situ nano-composite fabrication of PADF with SiO₂ is as follows: 0.3g of [PO(OH)₃]₂CC₆₀ was dissolved into 2.4 ml of CH₃CH₂OH and 1.2ml of H₂O, and then added and well mixed with 0.6 ml of TEOS. The solution was kept in a 60°C oven for 18h. The mixed solution turned into a deep-brown solid matter which was thought to be a nano-composite of [PO(OH)₃]₂CC₆₀ and SiO₂. The mole ratio of [PO(OH)₃]₂CC₆₀ to SiO₂ was adjusted to 1:8.

Infrared spectra were recorded as a KBr pellet using a Nicolet 360 FT-IR spectrum. The morphology of this sample was observed using SEM (JEOL JSM-6700F).

2.2 Proton conductivity

After drying the powder of PADF, and its nano-composite in a 50°C vacuum oven over P₂O₅ for two days, the green pellets (4 mm in diameter and 0.3-1 mm thick) of these samples were formed using a cold-pressing technique at a pressure of 230 MPa for 60 sec. Silver paste was applied on both sides of the pellet as ionic blocking electrodes. Conductivity was determined by using a.c. impedance method using a Solartron 1260 impedance analyzer in the frequency range of 10 Hz-10 MHz at an oscillation amplitude of 10 mV. The temperature was controlled using a thermostatic chamber and R.H. was adjusted by introducing a mixture of dry and water-saturated air in an appropriate ratio. The temperature and R.H. were monitored using a digital thermo/hydro meter placed beside the sample pellets.

3 Results and discussion

3.1 Infrared spectroscopy

The IR spectra for PADF and its nano-composite are shown in Figs. 1(a) and 1(b), respectively. Figure 1(a) shows a strong and broad peak at 3390 cm⁻¹ and a small shoulder at 3213 cm⁻¹, which correspond to the stretching vibrations of O-H from water and from P-O-H, respectively. The strong and broad peak at 1210 cm⁻¹ and a pair of peaks at 1077 and 1042 cm⁻¹ are assigned to P = O and P-O, respectively. There is a very strong peak at 1723 cm⁻¹ due to C = O absorption. The hydrolysis process conducted in the NaOH solution may produce some -OH groups on the same fullerene cage, which may lead to the conversion of vicinal hydroxyl groups to corresponding ketone structure with a ring opening via a pinacol-type rearrangement, as reported by Li et al. and Chiang et al. Thus PADF produced in this way is thought to be composed of one functional group of [PO(OH)₃]₂CC₆₀ and some -OH groups attaching on the fullerene cage. In addition, there is a shoulder centered at 2936 cm⁻¹, which is attributed to C-H vibrations. This may be caused by C-H bonding produced by a reaction of C₆₀ with CHCl₃ used as a solvent.

Figure 1 (b) shows the spectrum for the nano-composite of PADF with silica. It shows a strong and broad peak at 3410 cm⁻¹ and a small shoulder at 3250 cm⁻¹, which correspond to the stretching O-H vibrations from water and P-O-H, respectively. However they are shifted about 30 cm⁻¹ to higher wave-numbers than those of PADF. This shift may be attributed by Si-O-H groups since silica should have this group on its the surface. The triplet peaks at 2990 cm⁻¹, 2950 cm⁻¹ and 2920 cm⁻¹ are attributed to C-H vibrations. They are much stronger than the peaks in Fig. 1(a), and are probably due to some of the TEOS had not been fully hydrolyzed into SiO₂. There is a remarkable change in the wave-number range between 960 cm⁻¹ to 1230 cm⁻¹ due to the silica involved. The strong and broad peak around 1060 cm⁻¹ to 1100 cm⁻¹ is probably due to O-Si-O, while the P = O (1210 cm⁻¹) and P-O (1077 cm⁻¹ and 1042 cm⁻¹) in Fig. 1(a) for PADF are not distinguishable in Fig. 1(b). This indicated the formation of a nano-composite in which PADF and SiO₂ are bonded with a certain chemical interaction.

3.2 SEM observation

The morphology of this nano-composite observed by SEM is shown in Fig. 2(a). One may see that the morphology for this in-situ produced nano-composite of [PO(OH)₃]₂CC₆₀/SiO₂ is homogenous and without any
observable distinguished particles of [PO(OH)₂]_xCC_\text{ad} and SiO₂. For comparison, the as prepared PADF is also show in the Fig. 2 (b). The simple mixture of PADF with SiO₂ is shown in Fig. 2(c).

The sample of Fig. 2(c) was produced as follow: after mixing the water solution of PADF and SiO₂ powders, the mixture was stirred at 80°C for overnight. It was then dried at 60°C oven for one day. The powder was crushed using a mortar and it was then washed with water 3 times.

It is clear from Fig. 2(c) that the morphology of this sample is very different from the in-situ produced nano-composite, with large SiO₂ particles and the [PO(OH)₂]_xCC_\text{ad} adsorbed on its surface (as indicated by arrows in the figure).

The sol-gel reaction for the nano-composite from PADF and TEOS is thought to include the hydrolysis and the condensation as follows:

\[
\text{Hydrolysis:} \\
= \text{Si-OEt} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{EtOH}
\]

\[
\text{Condensation:} \\
= \text{Si-OH} + \text{HO-Si} \rightarrow = \text{Si-O-Si} = + \text{H}_2\text{O} \\
= \text{Si-OEt} + \text{HO-Si} \rightarrow = \text{Si-O-Si} = + \text{EtOH} \\
= \text{Si-OH} + \text{HO-P-C-C}_n \rightarrow = \text{Si-O-P-C-C}_n + \text{H}_2\text{O}
\]

It is thus thought that this composite has a linkage like -P-O-Si-(O-Si)_n-P- (n > 0) forming from the phosphoric acid by losing one proton to combine with one or several -O-Si-O-. The surface molecule of Si is combined with -O-H. Thus there are two kinds of protons in this nano-composite, one is highly dissociable proton (\text{PO(OH)}) and other is less dissociable proton (Si-OH).

3.3 Proton conductivity

The proton conductivity of [PO(OH)₂]_xCC_\text{ad} and the nano-composite of [PO(OH)₂]_xCC_\text{ad}/SiO₂ (mole ratio of 1:8) are estimated from the ac impedance measurement. The typical Cole-Cole plots for the nano-composite, measured at 25°C under R.H. of 46% and 57% are shown in Fig. 3. The thickness of the sample is 0.8mm and the area is 125.6mm².

The plot is characteristic of ionic conductor with an interfacial impedance at low frequency, followed by a semicircle. The intersection of the semicircle on Z’ was obtained by the curve fitting of the semicircles which is considered to be the bulk ionic resistance of the sample. The electronic resistance of the sample was confirmed as being more than 3 orders of magnitude higher than its ionic resistance. The proton conductivity (σ) is calculated from the ionic resistance (R) of the sample using the formula of

\[
\sigma = (1/R)(L/S)
\]  

(1)

where L and S are the sample thickness and area respectively.

![Fig. 2](image1.png)

**Fig. 2** The SEM of the powder samples, (a) the in-situ prepared nano-composite of [PO(OH)₂]_xCC_\text{ad}/SiO₂ (X500.000), (b) [PO(OH)₂]_xCC_\text{ad} (X50.000) and (c) the simple mixture of [PO(OH)₂]_xCC_\text{ad} and SiO₂ (X3000), the adsorbed [PO(OH)₂]_xCC_\text{ad} is indicated by arrows.

![Fig. 3](image2.png)

**Fig. 3** Typical Cole-Cole Plots for the nano-composite measured at 25°C under R.H. of 46% and 57%.
Proton conductivity plotted with R.H. is shown in Fig 4. The logarithmic proton conductivity of both samples is increased linearly R.H. at 25°C. The linear increasing of the logarithmic proton conductivity for PADF was discussed in our previous paper.\textsuperscript{10} The similar linear increasing was reported by Park \textit{et al.}\textsuperscript{14,15} for a composite of the silicon oxide doped with silicotungstic acid and silicophosphate-HClO\textsubscript{4} gel.

One should be noted that the conductivity of the nano-composite show about 10\textsuperscript{7} S cm\textsuperscript{-1} under the low relative humidity at about 10\%, while the conductivity for [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} was too low to be measured. The nano-composite increased its proton conductivity to about 3 \times 10\textsuperscript{4} S cm\textsuperscript{-1} under 40\%, which is about one order of magnitude higher than that for [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} under the same R.H. The increasing in proton conductivity under low relative humidity is thought to be that silica acting as a proton conductor, since the surface of the SiO\textsubscript{2} is composed of SiOH which may donates protons. Also the physically adsorbed water in the nano-composite may increase the proton mobility.

On the other hand, under the high humidity (>60\%), the conductivity for the nano-composite is lower than that of [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60}. This is due to a decreasing in highly dissociable protons on phosphoric acid groups, since the bonding of -P-O-Si- may take one proton from [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60}.

Other two nano-composites with the mole ratio of [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} to SiO\textsubscript{2} as 1:4 and 1:2 were also synthesized in the same way. The proton conductivity at different R.H. was measured. The results are shown in fig. 5. For comparison, the [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} sample and the nano-composite with the mole ratio of 1:8 are also shown. The proton conductivity for higher doped [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} (1:4 and 1:2) at low R.H. is lower than that of 1:8, while the conductivity at high relative humidity is higher. This confirmed that the surface proton on SiOH may enhance the proton conductivity under low R.H. Otomo \textit{et al.}\textsuperscript{16} had discussed SiO\textsubscript{2} surface proton may strongly influence the conductivity in CsH\textsubscript{2}PO\textsubscript{4}-silica composite.

The temperature dependence for the [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} and its nano-composite (mole ratio of 1:8), measured in the dry atmosphere with the dew point below -50°C in the temperature range from 18°C to 150°C, are shown in figure 6. The proton conductivity is too low to be measured for [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} below 70°C. The plots for [PO(OH)\textsubscript{2}]\textsubscript{3}CC\textsubscript{60} shows straight line and the activation energy (E\textsubscript{a}) estimated from the slope of log(\sigmaT)-1/T is 1.52 eV, which is much larger comparing with the one measured in the humidified atmosphere in our previous paper.\textsuperscript{10} The activation energies under each R.H. of 40\%, 50\% and 75\% are 0.52, 0.93 and 1.08 eV respectively. The plots of log(\sigma) vs. 1/T did not show the linear relationship for the nano-composite. It is probably due to the loss of the physically adsorbed water while the temperature is higher than 50°C. It is interested to note that the plots

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{proton_conductivity_vs_RH.png}
\caption{Plots of proton conductivity vs. R.H. for PADF (●) and the nano-composite (1:8) (▲).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{log_sigma_vs_1000_T.png}
\caption{Plots of log(\sigma) vs. 1000/T for PADF (■), and the nano-composite (1:8) (▲) in the temperature range of 18°C to 150°C under dry atmosphere. ▲ is measured from 150°C to 70°C for the same sample of ▲ after being measured from 18°C to 150°C. The estimated activation energies are 1.52 eV for PADF and 0.75 eV for the nano-composite (1:8) measured from 150°C to 70°C. The arrows indicate the temperature increasing and decreasing when measured for the nano-composite.}
\end{figure}
of log(σ) vs. 1/T for the nano-composite measured from high temperature of 150°C to 70°C, shows the straight line and the activation energy is estimated as 0.75eV. The nano-composite shows the lower activation energy probably because the silica provides some sites suitable for the proton conduction.

4 Conclusion
The nano-composite of PADF with SiO₂ was synthesized using in-situ reaction of [PO(OH)₂]₃CC₆₀ with TEOS. The proton conductivity of the nano-composite is higher than [PO(OH)₂]₃CC₆₀ in the humidity range below 50%, which is thought to be due to the fact that there are more proton conduction sites contributed by silica as well as due to the physically adsorbed water molecules. The lower activation energy of the nano-composite (0.75eV) than [PO(OH)₂]₃CC₆₀ (1.52eV) supports this description.

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References