THERMAL AND ELECTRICAL PROPERTIES OF "LIQUID" NANO CARBON AND ITS APPLICATIONS IN FUEL CELL TECHNOLOGY

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Abstract

In the previous study [7] , we conducted the study of chemical top down process which seems to provide better efficiency and better cost saving than the physical top down in the fabrication of nano scale , especially, when applying to carbon materials. It is found that the chemical top down performs effectively with multiple attachments of electrolytic groups onto the surface of the carbon powder by diazo coupling reaction. As a result, we are able to isolate the nano scale of carbon particles with strong polar solvents such as water and believe that it is due to electrostatic repulsive force between same sign charges existing in the polarized electrolytic groups... In the present study, we found that the cleavage of azo bond in the coupling product can occur above 110oC in ambient condition but it can also escape the thermal decomposition by a nano composite structure using specific emulsion polymer as binder matrix. Electrolytic groups which carry charge from ionization are speculated to reduce electron transport but enhance proton transport capability of carbon material, have successfully demonstrated a proton exchange membrane (PEM) which exhibits better heat resistance and higher current density than the commercial PEM Nafion product in the PEM fuel cell application. The multiple coupling product exhibits a core-shell structure composed of a nano scale hydrophobic core and electrolytic shell, showing apparent "solubility "and named as "liquid" nano carbon (LNC).

1. INTRODUCTION

"*Nanotechnology*" is a terminology to determine the science and technology related to the substance having scale below 100 nanometer according to the Nanotech Conference 2004 held in March in Boston USA [1] . The conceptual vision of nano scale materials had been announced by Richard Feynman in 1959 [2] but the real works was recognized since the discovery of carbon nano tube by Ijima in 1991 [3]. So far, in general, there are two ways which have been known to approach nano scale fabrication process:

"Physical top down" utilizes high energy to break down the large mass into the nano scale by weakening the intramolecular interaction but enhancing intermolecular interaction to stabilize the nano structure. The well known sputtering, vacuum sublimation, pulverizing process with and without chemical aids are typical examples of the physical top down. Regarding the semiconductor technology, the photolithography [4] is one among principle tools producing large number of tiny chips from a single mother of semiconductor wafer and it can be considered as physical top down.

"Bottom-up" builds nano scale from the arrangement of basic components in the atomic level. These processes also require high energy and vacuum technologies to create free radicals from gas phase materials , then the different categories of free radicals can react to each other to form new compound into the desired nano scale products. MOCVD, Plasma Enhancement CVD, Low Pressure CVD, MBE. . .etc are major tool of bottom –up . Process of the carbon nano tube is an example of a bottom –up in which the free radical of C adsorbed on the catalytic metal surface and grows the tube structure. In the territories of nano fabrication, dip pen lithography [5] is a known technique which is considered as bottom up process as it can print nano components from sulfur atom.

1.1) Novel Concept of Chemical Top Down Process

In the previous study, we approached a new type of top down process producing nano scale particle by multiple attachment of suitable electrolytic groups onto the surface of targeted materials, which, upon ionization (by E field or by strong polar solvents), can perform the electrostatic repellence between same sign charge. The product of this concept should be well dispersed in strong polar solvents such as water and shows the ion- induced hydrophilicity and no need to use heavy duty mechanical power to break them down into desired nano scale particles. This process is considered as *chemical top down process*. Carbon materials are the first choice for this approach as it has attracted a lot of attention from the structural engineering besides the fact that carbon black , graphite are composed of loosen layer structure which might be easily broken down into more basic level useful for the next formation of novel materials .

Next, it is necessary to select the chemical reaction routes which can chemically attach desired functional groups to perform electrolytic particles and then create nano scale particles.

USP 5554739 and 5922118[6], demonstrated unique carbon black material for inkjet colorant application by attaching water soluble anchor group onto it to form black particles stably suspending in water. The attachment occurs via a diazo coupling reaction using primary amine precursor containing desired functional groups wanted to be on black carbon ring system. In aqueous solvents, the commercial products; Cabojet 200 and Cabojet 300 is reported to exhibit aqueous aggregate having average particle size in the vicinity of 130nm and they are very closed to nano scale material but not quite yet [1]. In the previous study [7] , we repeated the coupling process on the same material for multiple times expecting that the multiple coupling process could increase the concentration of electrolytic groups on the invidual carbon particle surface to increase more repellent force exerted between same sign charge particles to stabilize nano scale in suitable environment . From that study, it is already observed that the multiple coupling products show increased water solubility. The term "liquid" nano carbon (LNC) is originated here to determine nano scale particles of carbon which look apparently soluble in strong polar solvents.

In this report, for the convenience of the terminology expression, Dn term indicates the product from the *n*th diazo coupling cycle , thus, D0 is the carbon black raw material which has not been exposed to any diazo coupling process yet, D1 is the product of the 1st diazo coupling reaction, D4 is the product of the 4th diazo coupling reaction etc . . and we chose D4 as standard nano material for the entire study in this report.

In the present study, we investigated the effect of the number of diazo coupling cycle on the morphology, the thermal and electrical properties of surface modified carbon black, confirming that electrical measurement can give some insights for the effect of the multiple diazo coupling processes. We also investigated the polymeric binder effect on the thermal and electrical properties of LNC, leading to a suggestion that a nano composite of LNC and aqueous emulsion polymers can be used as electrolyte membrane material[8],[9],[10],[11],[12].

2. EXPERIMENTAL PROCEDURE

2.1) Preparation of Carbon Black D_0

Carbon black was prepared by burning acetylene gas coming out from the reaction of water with calcium carbide. The fume product is quenched with cooled jacket water and collected in a magnetic stirrer water vessel. The primary aggregate of carbon black was purified respectively with acid, base, organic solvents (toluene, acetone), and baked at 140°C at least for 4 hrs in a convection oven and then at 300°C for 45 minutes in a furnace.

2.2) Preparation of LNC

The carbon black starting material D_0 prepared in 2.1) was exposed to 4 times of diazo coupling process using sulfanilic acid (p-amino sulfonic acid) as coupling agent, referring the previous report [7]. p-amino benzoic acid was also used to investigate the LNC having –COOH as electrolytic group. The forming of diazo coupled products was confirmed with the significant increase of water solubility and FtIR spectroscopic measurement.

2.3) Testing Procedure

i) Ft IR measurement was carried out with FtIR Tensor 37 (Bruker) equipment.

ii) TEM measurement using JEOL Model 1010

iii) XRD measurement using Siemens Model D5000

ii) Thermal analysis was measured using STA 409 PC-Nietzsche equipment.

iii) Electrical resistivity measurement was conducted as following

A pair of silver paste electrode spacing 1cm from each other was screen-printed on the top of 250 micron thick plain paper and air dried for several hours.

LNC was milled without milling media in a glass jar containing distilled water for 2 hours to form black slurry having solid content of 7.5% wt, then casted on silver electrode by wound wire bar to form 10 um thickness (measured by a stylus profiler (KLA Tencor)) after being baked at 100°C for 2 hours in a convection Blue M oven (VWR). The surface resistivity of LNC was directly measured using in-house 4 point probe tester.

For the testing of (LNC/polymer) composite, selected aqueous emulsion polymers were added into the milling jar with adjusted suitable viscosity for good film coating and the test film was prepared by the same way above described.

2.4) Thermal Annealing Process

Thermal annealing process of LNC was carried out in an oven equipped with high heat resistant ceramic materials including oven cover, heat resistant layer, heat resistant ceramic tube containing coil heater, heat controller and a Pyrex glass annealing tube. The diameter of the Pyrex glass tube is about 25mm, active heating length is about 40 cm and the entire length of the tube is about 70cm. The heating system (heater and controller) can provide a well controlled temperature to the annealing chamber up to 1200°C.

In order to carry out the thermal annealing process, first, weighed D_4 (from sulfanilic acid) in a Pyrex glass tube was inserted into the heated zone of the heating chamber filled with N_2 (flow rate 0.5 l/min.) , then the heat controller was set at targeted annealing temperature and the heating was started. The test tube sample was kept at the target temperature for 30 minutes. At the end of annealing, the tube was slowly moved out of the heating zone to be cooled off , then N2 source was turned off . The annealed LNC weight was measured again and the electrical resistivity was tested.

3. RESULTS AND DISCUSSION

3.1) TEM image

Fig. 2 exhibits TEM image of the D1 (a) and D_4 (b) in the powder form. One can recognize that in the dried stack of powder form, there is no signals revealing the difference between D1 and D4, suggesting that the multiple coupling process won't affect the size of primary individual particles. It may be believed that multiple coupling processes provides more sufficient number of the electrolytic group needed for the aggregate size reduction compared to the single cycle of coupling process. In reality, there is no quantitative way to determine exactly the number of electrolytic group obtained through the coupling reaction. However, the study of electrical properties of LNC as functions of number of diazo coupling cycle in the present report could give some insights for the multiple diazo coupling effects.

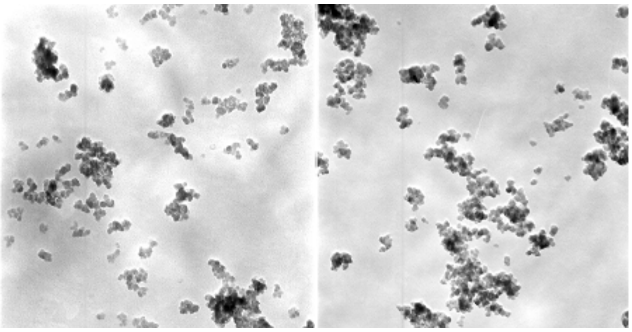
(a) (b)

Fig.*1 TEM image of D1 (a) and D4 (b)*

3.2) XRD

Fig.3 exhibits XRD patterns of various kinds of LNC from D1 to D6. The figure also displays the XRD pattern of the raw material D0 and the D6 product annealed at 1000C in an oxygen free environment (by purging N2 through the annealing furnace during annealing time of 3 hrs . The figure shows that the carbon black materials in the present study exhibits amorphous form. The multiple coupling processes does not substantially affect the morphology of the carbon as the raw material Do exhibits almost identical XRD patterns with other multiple coupling products D1, D4, D6. It should be noted that the amorphous form is strongly maintained even D6 is hardly baked at 1000C for 3 hours in an oxygen free environment (N2 was continuously purged in the annealing oven). In a separate study, we found that the hard bake of D6 in an oxygen rich environment causes a large weight loss of thermally annealed product , may be due to the oxidation.

3.3) Electrical Properties of LNC

3.3.1) Electrical resistivity as functions of number of diazo coupling cycle

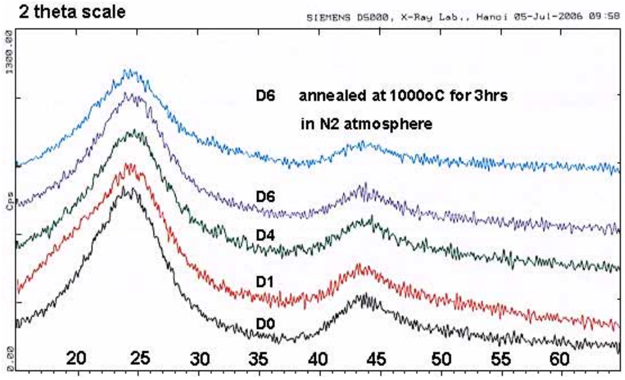

Fig.2*XRD patterns of various kinds of LNC*

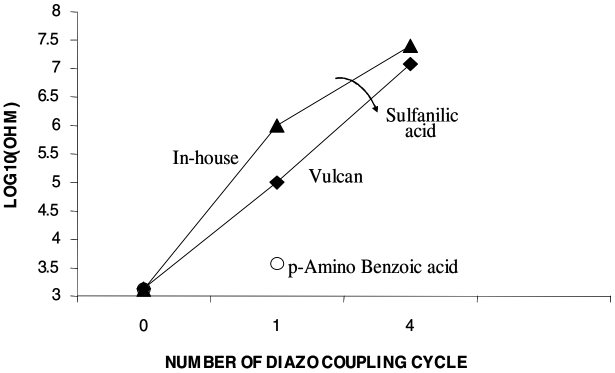

Fig.*3 Effect of number of coupling cycle on electrical resistivity*

Fig. 3 shows the electrical resistivity of various types of Dn products made out of D_0 (in-house) using sulfanilic acid as diazo coupling agent. For a comparison, Dn products were also prepared with commercial carbon black Vulcan XR 72C (Cabot Corporation). The measured data of the D_1 (-COOH) product using in-house carbon black D_0 was also plotted. It should be noted that all electrical measurement was done in the ambient condition (room temperature, 72% Rh). It is observed that the electrical resistivity of D_1, D_4 is much higher than that of D_0 in a magnitude of 10^3 and 10^4 X, respectively. Also, the electrical resistivity of D_4 is higher than D_1 at least 10 X. Even though, the Vulcan itself shows a bit more electrically conductive than D_0, the diazo coupled products of Vulcan still show the same trend with the in-house D_0, i.e., a significant resistivity increase was observed in multiple diazo coupling products. On the other hand, the D_1 (-COOH) product shows less changes in electrical properties compared to D_1 ($-SO_3H$), agreeing well with the fact that $-SO_3H$ group is known to exhibit higher protonation efficiency than the –COOH group. If we assumed that multiple diazo coupling cycle could increase the density of electrolytic group on the individual carbon particle, then the electrolytic group $-SO_3^-$ or $-COO^-$ must be responsible for the electrical conductivity reduction in the carbon black due to the increased proton transport, or at least the sulfonic acid or sulfonic acid sodium salt, the carboxylic acid , or the carboxylic acid sodium salt had significant interference with the electron conduction of the carbon black system itself . The strong dependence of electrical resistivity on the number of diazo coupling cycle suggests that electrical measurement could lead to some insights to the effect of multiple coupling processes.

3.3.2) Thermal annealing effect of LNC

Fig.4 exhibits the electrical resistivity of D_4 (using sulfanilic acid) annealed at different temperature from 132°C to 700°C in atmospheric environment for 30 minutes. Again, all of electrical test was done at ambient condition (room temperature and 70%RH). It is observed that the electrical resistivity tends to rise may be due to the dehydration then drop after the annealing temperature passes 140°C. After 400°C, the drop in resistivity starts slowing down and almost stays unchanged after 500°C.

In the same Fig.4, electrical resistivity of several annealed LNC was measured at higher humidity (100% RH) condition. It is observed that at high humidity, the electrical properties of LNC are independent with annealing temperature, suggesting that it is more dominated by the ionic transport.

Further measurement of FtIR (Fig. 5) on annealed D_4 samples reveals that the peaks appeared at 1160-1200 cm^{-1} and 1330-1380 cm^{-1} (representing $–SO_3$) and the peaks appeared at the vicinity of 1030-1080 cm^{-1} and 1110-1150 cm^{-1}, (representing –N=N) , only clearly appear in fresh D_4 and D_4 samples annealed at temperature lower than 400°C. These functional groups completely disappear in the samples annealed above 400°C; their IR spectroscopic charts just look the same with the D_0. Next, Fig. 6 shows the DTA/TG data of D_0 and D_4. In the D_4 product, the thermal reaction starts being observed in the vicinity of 110°C whereas D_0 did not show any signals until 600°C.

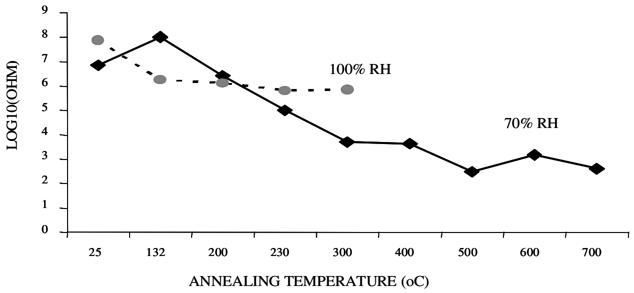

Fig.*4 Annealing effect on electrical properties of LNC*

From the above described evidences, it is observed that

a) the D_4 is less thermally stable than the raw material D_0

b) Electrolytic group $–SO_3H$ starts leaving off the carbon core at about 110.2°C and completely disappears above 500°C. The thermal instability of D_4 could be due to the cleavage of azo bond –N=N- during the annealing process. The cleavage of azo bond –N=N- , causes the LNC products lost their electrolytic group $–SO_3H$ and thus gaining back the electron conduction properties .

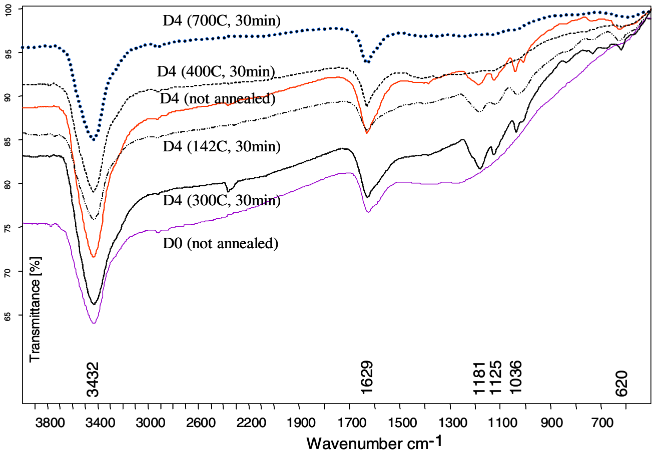

Fig. *5 FTIR spectrum of D4 annealed at various temperature*

3.3.3) Binder effects

As LNC product is well dispersed in aqueous environment, the aqueous emulsion polymers are preferred to give a uniform dry film in which the nano scale of LNC is still maintained. Several different kinds of aqueous emulsion polymers and hydrophobic cross linking poly urethane (PU) were tested. All of the measurement was carried out at room temperature and 72 % RH condition. From this result, it is able to classify the behavior of polymer into 3 groups

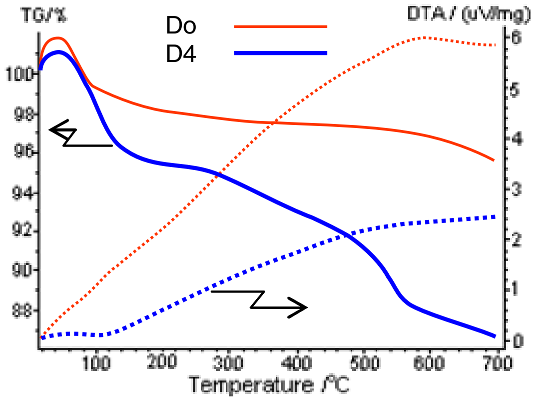

Fig. *6 DTA/TG data of LNC*

Group A: The polymer exhibits the increased electrical resistivity of nano composite with binder content. Group A comprised of cross linking poly urethane (PU), emulsion polymers (43N40, 316N30 from CHEMCOR), emulsion polymer products from KOVA, in-house emulsion copolymer 2 (in-house Copo2).

Group B: The polymer shows no effect on resistivity such as the in-house emulsion copolymer 1 (in-house Copo1); electrical resistivity is not affected by binder content.

Group C: The polymer exhibits the decreased resistivity with binder content such as the in-house copolymer 3 (In-house Copo3).

At binder content < 50% wt, the electrical resistivity of nano composite is dominated by LNC. However at the binder content greater than 50% wt, the electrical resistivity is believed more dominated by the binder. Based on these data, it is speculated that the Group A and Group B is composed of conventional insulative polymers. The unique properties of Group C suggest that the polymer is a more conductive polymer, compared to other polymers of Group A and B. However, it should be noted that most of emulsion polymers containing a large quantity of ionic surfactants to stabilize the monomer emulsion before polymerization and it could affect the electrical properties of the LNC composite at well . The detailed study of the nature of electrical transport mechanism in the nano composite will be discussed in another report.

Next, the binder effect on thermal properties of LNC was investigated with DTA/TG data measurement and the results are illustrated in Fig. 7. In this case, the nano composite was formulated with LNC / polymer ratio = 1/1 by wt and the study was carried out with two types of emulsion copolymers; in-house Copo2 and in-house Copo3. LNC exhibits exothermic peak at 110.2°C revealing the thermal instability of LNC D_4 as above mentioned. However, it is noteworthy that this peak is completely disappeared when D_4 is blended with in-house Copo3 and the mass loss of the composite film also becomes flat between 0°C and 350°C. The flatness of the DTA/TG curve may reflect a recompansation in mass loss between LNC and polymeric binder. As previously mentioned, the aqueous hydrophobic emulsion polymers maintain the nano scale of LNC particles in the film thus could perform strongly the interaction between the chemistry of LNC and polymer, which might reflect in the thermal stabilization effect of LNC by polymeric binder. On the other hand, the in-house Copo2 reversely, didn't show any improvement on thermal stabilization but further deterioration with greater mass loss. In the same Fig.7, DTA/TG data of Nafion (from Nafion117) was also shown. Nafion shows exothermic peaks in the vicinity of 100-150°C and starts gradually loosing mass even at low temperature zone between 100°C and 450°C; the mass loss in Nafion is almost completed at about 550°C. Fig.8 summarizes the electrical resistivity of the LNC nano composites, measured at various temperatures. In this case, 4 composites were formulated. These are D_1, D_4 blended in in-house Copo1 and in-house Copo3. It is observed that the nano composite comprised of D_4 blended in the in-house Copo1 shows the highest resistivity with stable performance within the limitation of temperature measurement (180°C). On the other hand Nafion 117 shows the second high resistivity. It should be noted that the Nafion 117 starts deform after 80°C; the film becomes dark brown and completely destroyed at 120°C, making the measurement unavailable. Other nano composite films show relatively stable electrical properties and mechanical strength during the temperature range of measurement between room temperature and 180°C without any signals of physical changes or damage of the film. Actually, further heating test was done up to 350°C and shows no physical damage of the composite film.

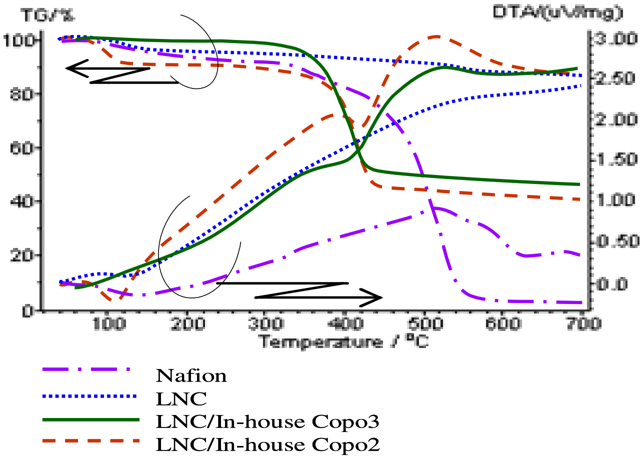

Fig.*7 DTA/TG of nano composite*

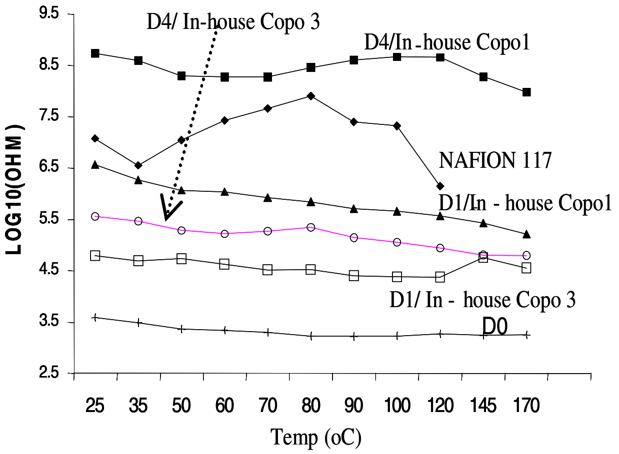

Fig. *8 Electrical resistivity of the nano composite as functions of temperature*

3.3.4) PEMFC performance of LNC nano composite

Next, a PEM FC was formulated to test out the PEM performance of the LNC nano composite. In this case, a PEM fuel cell structure is composed of liquid fuel diffusion layer (Toray Carbon Paper TGPH-060 purchased from E-Tek product) over coated with Vulcan XR72C dispersion. In anode site, electro catalyst layer is composed of dual layer of sputtered Pt (10nm thick) and sputtered Ru (5 nm thick). In cathode side, electro catalyst layer is a 10nm thick Pt layer directly sputtered onto the Vulcan XC72R dispersion layer .

The membrane is composed of 50% D_4 embedded in 50% in-house Copo3 ultrasonically mixed for 5 minutes , then brush painted on the top of the electro-catalyst layer and baked in the same oven for 30 minutes at 80^oC . The active surface area of the membrane is about 4 cm^2. The PEM thickness was detected to be around 168 um and is equivalent to that of the Nafion 117 membrane. Fig. 9 shows the V-I characteristic curves of the PEM made out of D_4/Copo3 composite compared to commercial Nafion 117 product using the same electrode materials with the LNC composite fuel cell . The fuel source is composed of 3% methanol in DI water . One can recognize that the nano composite PEM shows higher current density than that of Nafion 117. Fig.10 shows power efficiency curve of the nano composite PEM compared to that of the Nafion 117 PEM in the same PEMFC configuration. The LNC nano composite PEM shows 2X higher power efficiency than that of Nafion PEM.

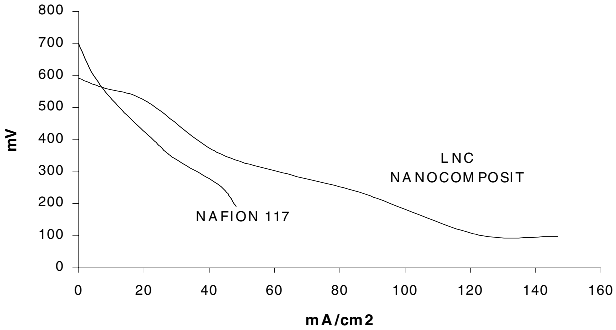

Fig. 9 *V-I characteristic curves of the nano composite compared to the Nafion 117 pem*

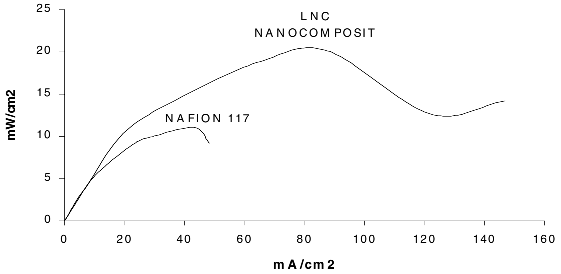

Fig. 10*Power efficiency curve of pem fuel cell utilizing lnc composite membrane and nafion membrane*

Besides the above electrical performance, the PEM FC utilizing LNC nano composite exhibits life time exceeding 3.5 months with continuous feeding of aqueous liquid fuel to light up the white LED light bulb . The cell just looks like "sleeping" whenever the liquid fuel is ran out and starts working again when the membrane is wetted with a few drops of liquid fuel.

4. CONCLUSION

It can be concluded that

a) The electrolytic groups –SO_3H, -COOH are main drivers for the chemical top down process, the reduction of aggregate size , the electron conductivity , and the enhancement of the proton transport properties of carbon black

b) The linking of electrolytic group onto the carbon system occurs via azo bond –N=N- which is thermally unstable. However, the interaction between specific emulsion polymers when maintaining the nano scale of LNC could improve the thermal stability of the nano composite.

c) Actually, the nano composite PEM exhibits suitable PEMFC performance, at least equal to or superior than that of the Nafion 117 in terms of current density and power efficiency.

d) The LNC nano composite also exhibits superior heat stability (up to 350^oC) over the Nafion 117 PEM (80^oC)

e) The LNC nano composite PEM exhibits a shelf life exceeding 3.5 months with continuous feeding of aqueous methanol fuel source.

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Khe Nguyen received his BS in polymer science from Tokyo Institute of Technology (TIT) (1977) and his PhD in Information Physics from TIT (1982). Since then he had worked in the Research Laboratories of Dai Nippon Ink (Tokyo), Eastman Kodak (NY), Ricoh (San Jose, CA), Hewlett-Packard (Palo Alto), APTOS (Milpitas, CA), ICSensor (Milpitas, CA), and now,he is currently Lab Director of Saigon Hi Tech Park's Research Laboratories (Ho Chi Minh City, Viet Nam) . His work has focused on material science. He is granted 37 US patents in all fields of digital printing technology and semiconductor processing.