OVERVIEW OF “LIQUID” COAL AND ITS APPLICATIONS

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Abstract

In the previous study [1], we reported the achievement of nano scale particles of carbon black by multiple coupling of specific anchor groups having electrolytic functionality onto the same material. As a result, the pseudo products called as the “liquid” nano carbon (LNC) or “liquid” coal having average particle size down to the range between 20-30nm, can be isolated by water flush. The LNC product exhibits the thin film (400Ao thick) forming properties by solvent coating (for example using spinner , i.e. no need to use vacuum techniques,), and micro patterning capability useful for microelectronic device fabrication. We found that the surface modified carbon black with multiple coupling processes can be successfully utilized as intermediate materials for semiconductor wafer processing including the fabrication of dry etching mask for DRIE in MEMS devices, thermal management materials in nano chip . . . .

In another study [2], it is discovered that the electrolytic groups in LNC is the main cause for the significant reduction of the electrical conductivity of carbon black raw material. The LNC nano composite with suitable emulsion polymers exhibits remarkable proton transport efficiency with significant enhancement of thermal stability over wide range of temperature, measurable up to 350C in the ambient environment, suggesting that it can be used as proton exchange membrane (PEM) for PEM fuel cell. In fact, in a PEMFC configuration, the LNC nano composite PEM shows higher current density and 2X higher power efficiency than that of Nafion 117 which is well known in the PEMFC market. The PEMFC using LNC nano composite PEM also exhibits superior shelf life exceeding 3.5 months when an aqueous methanol liquid fuel system is continuously fed.

Over all, the surface modified carbon black has successfully met the applications of inkjet printing .The extended technology has generated a novel material which is LNC successfully leveraged into the area of micro electronic devices, energy technology and future printed electronics.

Introduction: Novel Concept of Chemical Top down Process and “Liquid” Nano Coal (LNC)

“*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[3] . The conceptual vision of nano scale materials had been announced by Richard Feymann in 1959[4] but the real works was recognized since the discovery of carbon nano tube by Endo in 1976[5] and it was revisited by Ijima in 1991 [6]. So far, in general, there are two ways which have been known to approach nano scale fabrication process: a) *“Physical top down”* utilizes high energy sources to break down the large mass into the nano scale by weakening the intramolecular interaction but enhancing intermolecular interaction to stabilize the nano structure and b) *“Bottom-up”* builds nano scale from the arrangement of basic components in the atomic level [7].

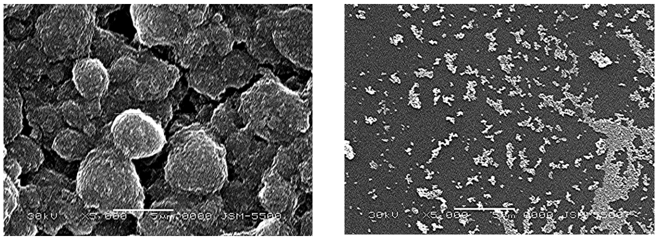
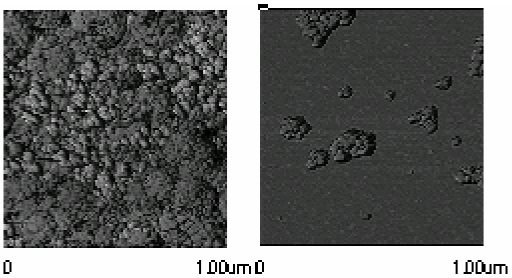

(a) Before (b) After

Figure 1 SEM image at X5000 of dry powder of carbon black before and after chemical modification

Recently, a new way of producing nano scale products had been investigated and it should be named as “Chemical *Top Down*” because nano scale is achieved by chemical functionality instead of mechanical forces. USP 5554739 and 5922118 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 are reported to exhibit aggregate having average particle size in the vicinity of 130nm and they are not quite nano material yet . In our works , we are interested in electrolytic anchor groups which can be polarized by ionization in strong polar solvents or even in an electrically biased environment and the repetition of the coupling process on the same material for multiple times expecting to maximize the



(a) Dried film (b) dried film flushed With a few drops of water

Figure 2*. AFM image of LNC (D4)*

concentration of electrolytic groups to help the particles carrying the same sign charge rebel more effectively each other to stabilize the nano scale . This kind of approach has gone beyond the inkjet printing ink applications because the product losses the water fastness strongly desired in hard copy technology. In fact, it is already observed that the more coupling cycle occurred; the coupling product shows more water solubility. The term “liquid” nano carbon (LNC) is originated here to determine nano scale particles of carbon which look “soluble “but not really a liquidified product. It should be noted right here that the multiple coupling process does not reduce the primary individual particle size but rather forms aggregate more easily broken down into nano scale in suitable polar solvents . For example, the attachment of highly polarizing groups such as sulfonic acid –SO3H or carboxylic acid –COOH under aqueous environment, can generate smaller aggregates from primary aggregate. Fig. 1 exhibits SEM image on the same magnification X5000, of dry powder of carbon black before and after chemical attachment of–SO3H, revealing a particle size reduction of roughly 30X from the raw material (roughly 2-3um) to the coupling product (100- 150nm) . Thus, the so called *multiple coupling products* (for example, the product from 4th coupling reaction) having AFM image showing in the Fig. 2 (a) for dried film and (b) for the dried film flushed with few drops of water . At least, it is found that the individual nano particle can be isolated with average particle size in the range between 20-30nm.

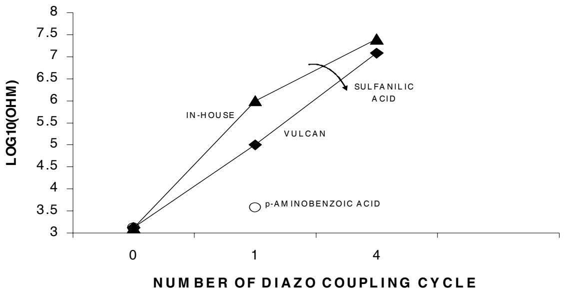


Figure 3. *Effect of number of coupling cycle on electrical resistivity*

The effect of multiple coupling reactions is observed by measuring the electrical resistivity of LNC at different levels of coupling as it is illustrated in Fig. 3. According to this result, it is suggested that the concentration of electrolytic groups as well as its chemistry strongly affects the electrical properties of carbon black. The electrolytic groups showing higher protonation efficiency exhibit more prominent effect (as seen in the case of sulfonic acid compared to carboxylic acid). The strong dependence of electrical resistivity on the number of coupling cycle suggests that electrical measurement could lead to some insights to the effect of multiple coupling processes.

Physical and Chemical Properties of LNC

Fig. 4 exhibits the FtIR charts of carbon black raw material (D0), 1st and 4th coupling product (D1 and D4 respectively) with –SO3H. It is recognized that the difference in IR spectrum of these samples, reveals the effect of multiple coupling process. It should be also recognized that the IR absorption peak appeared at the vicinity of 3400-3450 cm^{-1}, representing –OH, all exist in the raw material D0 and the product of D1, D4. However, the peaks appeared at 1160-1200 cm^{-1} and 1330-1380 cm^{-1} , representing –SO3 and the peaks appeared at the vicinity of 1030-1080 cm^{-1} and 1110-1150 cm^{-1} , representing –N=N , only clearly appear in the products but not in the raw material . The presence of –SO_3 group in the coupling products confirms the successful attachment of electrolytic group –SO_3H from sulfanilic acid molecule and explain the increased hydrophilicity of the carbon black. Besides the above groups, it is also observed the presence of the absorption peak at the vicinity of 1600 cm^{-1} representing conjugated bond C=C, 2900-3000cm^{-1} peak representing C-H bonding , 1200-1400cm^{-1} representing the IR vibration of –OH .

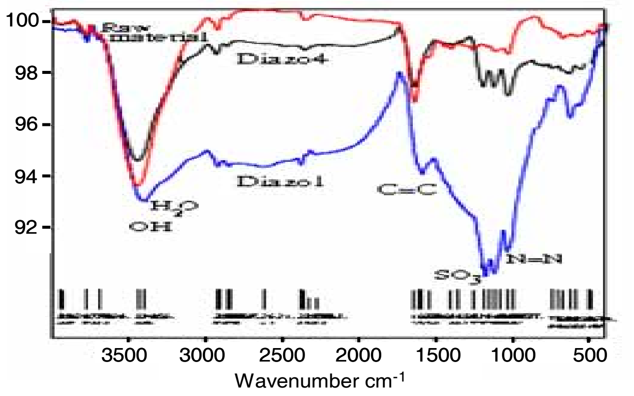


Figure 4. *FtIR spectrums of D0, D1, and D4*

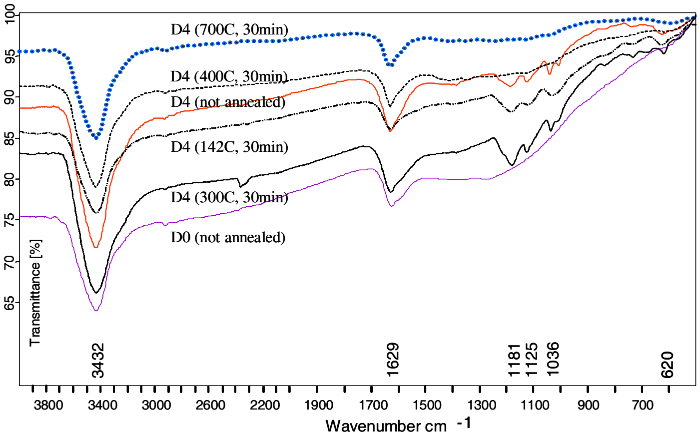


Figure 5. *FtIR spectrum of LNC (D4) annealed at various temperature*

Fig. 5 exhibits FtIR chart of the D4 annealed at various temperature for 30 minutes in the ambient environment , revealing that the peaks representing –SO_3H and the peaks representing –N=N only 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. Each sample may show several different peak temperature upon the impurities contained inside the sample.

Nano composite of LNC and emulsion polymer

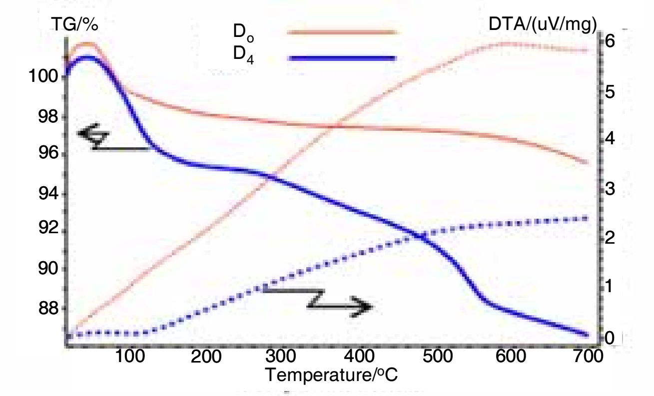


***Figure 6**. DTA/TG data of LNC (D4) and D0*

As LNC product is well dispersed in aqueous environment, the aqueous emulsion polymers are preferred to give a uniform dry film to form LNC nano composites in which the nano scale of LNC is still maintained. The binder effect on thermal properties of LNC nano composites 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 D4, previously 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. On the other hand, the LNC nano composite with in-house emulsion Copo2 shows adverse result with deteriorated thermal stability. Of course, the TGA results may reflect the recompansation effect of thermal behavior between that of LNC and that of emulsion polymer. However, this could be also due to the chemical interaction between these two parties. In the same Fig.7, DTA/TG data of Nafion (from Nafion117) [8] which is well known as proton transport polymer 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.

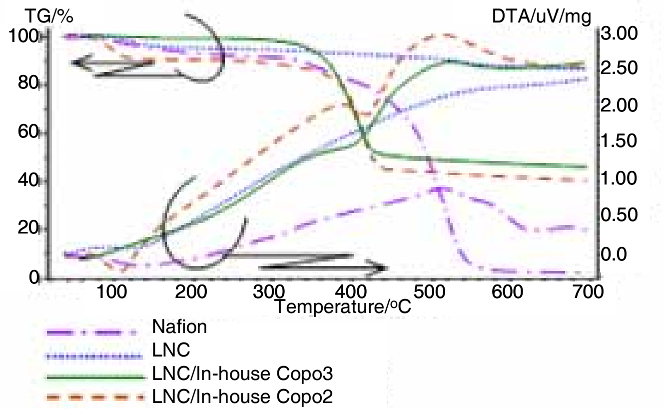


***Figure 7**. DTA/TG data of LNC nano composites with various emulsion polymers*

The binder effect in the LNC nano composites can be further confirmed by the measurement of electrical resistivity on a wide range of temperature. Fig.8 summarizes the electrical resistivity of the LNC nano composites, measured at various temperatures. Between RT and 180C in ambient condition. 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 (D4/Copo1) nano composite shows the highest resistivity with stable performance. 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 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 nano composite film.

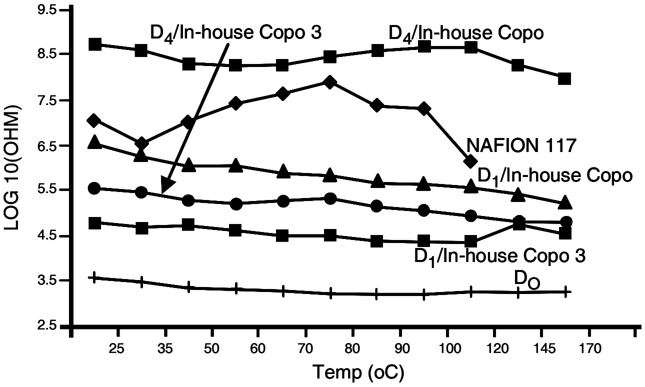


***Figure 8**. Electrical resistivity of LNC nano Composites at different temperature in ambient Environment*

From the above evidences, it can be summarized that the electrolytic groups is attached to the ring system of the carbon black through azo bond –N=N-, which cause the reduction in aggregate size, the reduction of electrical conductivity of the mother material, as well as the enhancement of proton transport efficiency . The coupling bonds are thermally unstable from 110C and the electrolytic groups completely leave off the ring at about 400C. However, a specific emulsion binder which forms suitable nano composite with LNC does show improvements of thermal stability upon the nano composite structure.

Applications of LNC

1. The stability of LNC in aqueous environment makes it available for inkjet printing [9] , especially with conductive ink for printed electronic applications
2. The nano scale of LNC makes it available to form thin film (thickness < 1um) by aqueous solvent casting process without using vacuum technology [1]

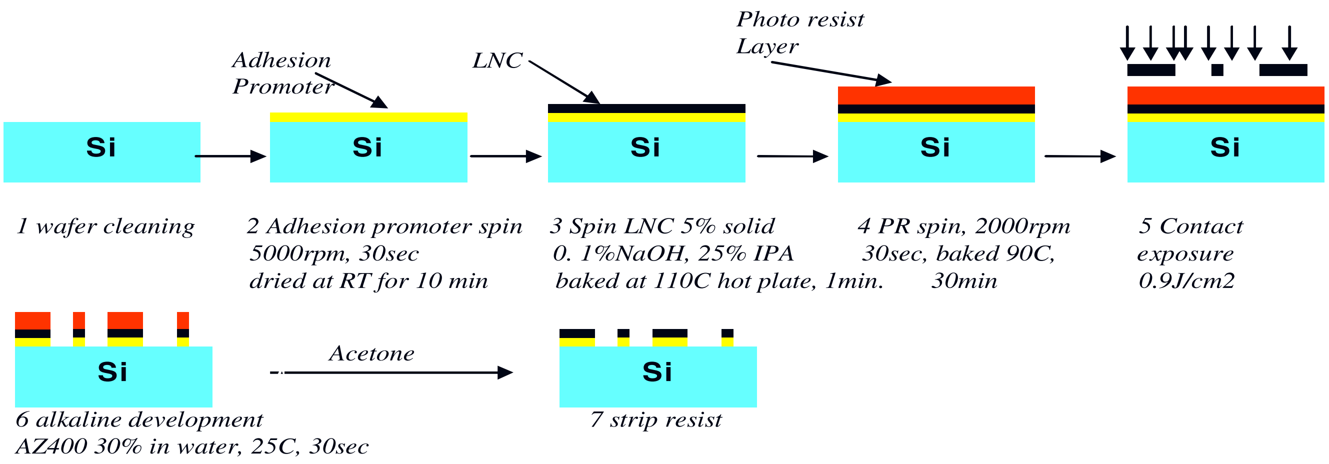
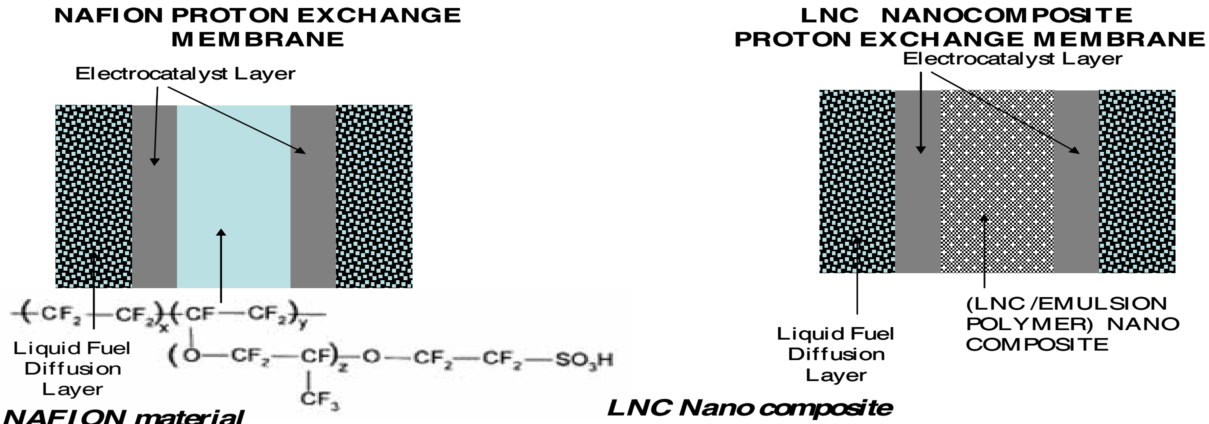


Figure 9. *Micro pattern imaging process of LNC*

3. The thin film of LNC can be combined with the conventional photolithographic technique to form micro pattern image on semiconductor wafer [1].
4. The thermal properties of LNC in conjunction with micro patterning capability can be useful to form heat resistant carbon mask for semiconductor wafer processing (such as deep RIE) and thermal management in nano chip [10]
5. LNC exhibits proton transport capability and can be used in battery technique such as fuel cell, microbial fuel cell , etc …[2]

Fig.9 shows the micro pattern imaging process of LNC in which a thin film of LNC spin-coated on a Si wafer is over coated with a positive photo resist by spin coater. The micro patterning image of LNC is successfully developed along with the photolithographic process of the positive photo resist. The development of image on LNC thin film can be explained by the solubility of LNC in alkaline developer: under exposure with UV light source, the positive resist becomes acidic and washed away with alkaline developer; the unexposed area protects LNC from alkaline attack. Development time, temperature, active components of developer should be major parameters to control the undercut of LNC layer. In order to use the LNC mask for deep etching with RIE, it is necessary convert the LNC mask into the carbon mask by heating it up to 400C for 1 hr in N2 atmosphere. The carbon mask is thermally stable and it can survive during the deep etching process with plasma (oxygen, CF4, SF6,). The carbon mask fabricated through LNC micro patterning process, thus, can be also used as thermal dissipation materials in nano scale chip which is expected to emit a huge amount of heat. Fig. 10 shows micro pattern image developed on LNC thin film with resolution of 1.5 um.



NAFION material

1. Non sticking
2. Poor film forming properties
3. Poor heat resistance (< 80C)
4. High water, fuel crossover
5. Expensive

LNC Nano composite

1. Excellent film forming properties
2. Excellent heat resistance (350C)
3. Low water/fuel crossover
4. Unexpensive
5 US Patent application pending.

Figure 11*. Comparison between LNC Nano Composite PEM and Nafion PEM in PEM FC*

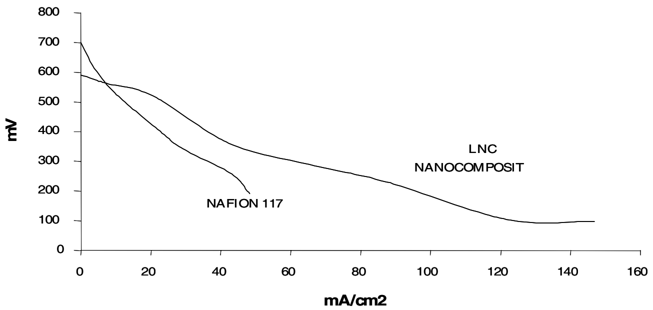


***Figure 12** V-I characteristic curves of the PEM made out of LNC Nano*

Composite compared to that of commercial Nafion 117

The principle of proton exchange membrane fuel cell (PEM FC) has been described in details somewhere in which the fuel source which can be either hydrogen gas or an aqueous solution of low alkyl chain alcohol can generate a proton when in touch with Pt catalyst sandwiched between an electron transport molecule and a proton transport molecule. It is assumed that the effective proton transport membrane in a fuel cell system must be able to transport the geminate proton out of the generation area as much efficient as it could in order to avoid the geminate recombination between electron and proton causing the electron lost in the outside loop. In reality, Nafion product from Dupont is a well known PEM product in the market. However, Nafion is a sulfonated Teflon polymer and exhibits poor adhesion properties against any substrate due to the low surface energy associated with fluoro chemistry [11] and thus, the film casting from Nafion solution is much harder to be successful. Several efforts [12] had been made to overcome these issues by changing the polymer backbone as reported for poly sulfone (PS), poly benzimidazole (PBI), poly ether ether ketone (PEEK) [13]. Even though, the challenges maintained in the balance between the density of proton transport functionality $-SO_3H$ and the hydrophobicity in the same film, leaving behind the major issues related to high fuel crossover, high water cross over, low methanol tolerance, ignoring the issues related to the material and manufacturing cost.

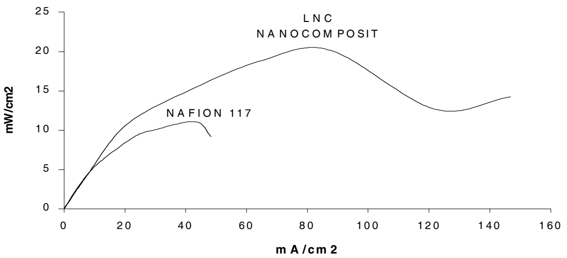


Figure 13. Power efficiency curve of PEM fuel cell utilizing LNC composite membrane and nafion membrane

Fig. 11 describes a comparison between NAFION 117 and LNC nano composite membrane for PEM FC applications. Fig. 12 shows the V-I characteristic curves of the PEMFC made out of D_4/Copo3 composite compared to commercial Nafion 117

product when an aqueous fuel containing 3% methanol was fed. It should be recognized that the nano composite PEM shows higher current density than that of Nafion 117. Fig.13 shows power efficiency curve of the nano composite PEM compared to that of the Nafion 117 PEM in the same PEMFC configuration. The nano composite PEM shows 2X higher power efficiency than that of Nafion PEM.

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.

Conclusion

It can be concluded that chemical top down is a novel nano fabrication process which is applicable for specific material such as carbon black to form nano scale carbon product named as "liquid" coal or "liquid" nano carbon (LNC). LNC is an intermediate material showing multifunctionalities that the mother material (carbon black) is not able to achieve such as

a) thin film forming properties without using vacuum technique
b) micro and nano pattern image forming useful for masking material in semiconductor wafer processing, and for thermal management in nano chip
c) Electrolytic groups exist on LNC exhibit particle repellent functionality helping to form nano scale aggregates. They also show proton transport capability as well as the capability of forming nano composite. Specific nano composite between LNC and emulsion polymer does show the improvement of thermal stability of LNC itself and make it useful as proton exchange membrane for fuel cell applications

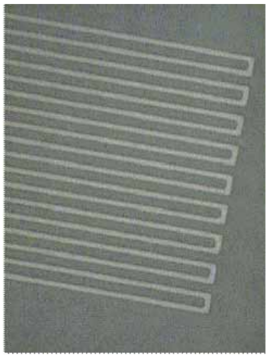


***Figure 10** Micro pattern*

Image developed on LNC,

Resolution 1um

References

[1] Khe et al, Digital Fabrication 2005 (Sept 2005, Baltimore), Proceeding , p.209
[2] Khe et al, Nanotech 2006 Conference (May 2006, Boston), Proceeding Vol.1, p.352 also see Khe et al. International Conference of Multifunctional Nano Composite (Sept 2006, Hawaii)
[3] Nanotech 2004 Conference , Planetary Session
[4] http://nvl.nist.gov/pub/nistpubs/calendars/techcal/2002/023809-tc.htm
[5] Endo, Proceeding of Nanotech 2006, Boston, May 2006
[6] S. Iijima, Nature, 354, 56-58, 1991
[7] George M. Whitesides and J. Christopher Love, "The art of building small", *Scientific American, Sept 2001, p.39*
[8] www.mitstanfordberkeleynano.org/.../

[9] USP 5554739 and 5922118
[10] http://www.indolink.com/SciTech/fr032504-050830.php
[11] US Pat 5,834,564
[12] G. Alberti, M. Casciola, Solid State Ionics, 145 (2001) 3
[13] K.D. Kreuer, J.Membr. Sci., 185(2001) 29

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Khe owns 37 US Patents and 5 proceedings in nanotechnology applications for energy, advanced materials and carbon nano tube.