Novel Electrolyte Membrane for Fuel Cell Utilizing Nano Composite
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ABSTRACT

In the previous study [1], we reported the achievement of nano scale particles of carbon black by multiple diazo 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) having average particle size down to the range between 20-30nm, can be isolated by water flush.

It is discovered in the present study that the electrolytic groups is the main cause for the significant reduction of the electrical conductivity of the carbon black raw material and believed due to the enhanced proton transport efficiency associated with the electrolytic chemistry. We reported here, a novel type of proton transport material comprised of LNC embedded in a polymer matrix to form proton conducting nano composite. The LNC proves stable nano scale [1] in aqueous environment and the nano composite demonstrated excellent film forming properties with a wide range of binders, especially, aqueous emulsion polymers and highly cross linking polymers. The nano composite also exhibits the excellent uniformity of membrane with well known coating process such as dip coating, spin coating, spray coating, roll coating, blade coating, rod coating, brush printing , inkjet printing. .

It is found that the nanocomposite shows stabilization of DTA/TG data curve over that of the single LNC itself. The nano composite also exhibits remarkable thermal stability over wide range of temperature up to 350C in the ambient environment compared to the Nafion 117, a well known proton exchange membrane (PEM) material in the PEM fuel cell [2] market. In fact, in a PEMFC configuration, the nano composite PEM shows higher current density and 2X higher power efficiency than that of Nafion 117. 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.

1. INTRODUCTION

USP 5554739 and 5922118 [3] , 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 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 aggregate having average particle size in the vicinity of 130nm and they are not quite nano material yet [4]. In the previous study [1], we selected the anchor group to be electrolytic which can form ionized particles in strong polar solvents or even in an electrically biased environment and then, 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 individual carbon particle surface and the particles carrying the same sign charge could rebel more effectively each other to stabilize the nano scale. It is already observed that the more diazo 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 could be noted right here that the multiple diazo coupling process does not reduce the primary individual particle size but rather forms aggregate more easily broken down into nano scale in suitable solvents.

In this report, for the convenience of the terminology expression, Dn term indicates the product from the nth 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. . . . Actually, the nano scale is only achieved after the 2nd diazo coupling process as the D1 product is still showing the aggregate form with average particle size above 100nm, well agreed with what is observed for Cabojet 200 and 300 products. So we decided to choose D4 as standard nano material for the entire study in this report.

In the present study, we investigated the electrical properties of surface modified carbon black as functions of the number of diazo coupling cycle, 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 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.

The principle of proton exchange membrane fuel cell (PEM FC) has been described in details somewhere [2] 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 gernimate proton out of the generation area as much efficient as it could in order to avoid the gernimate recombination between electron and proton [5] causing the electron lost in the outside loop . In reality, Nafion [6] product from Dupont is a well known PEM product in the market. However, Nafion is sulfonated Teflon polymer and exhibits poor adhesion properties against any substrate due to the low surface energy associated with fluoro chemistry [7] and thus, the film casting from Nafion solution is much harder to be successful [8]. Several efforts [9] 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). Even though, the challenges maintained in the balance between the density of proton transport functionality –SO3H 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.
In this report, we presented a novel type of electrolyte membrane material using a nano composite of LNC [10] and emulsion polymer. The nano composite looks promising in terms of high heat resistance and more choices for the binder design and selection. In this case, LNC is acting as proton transporter and polymeric binders tend to provide protection for LNC to meet the requirements of operating condition.

2. EXPERIMENTAL PROCEDURE

2.1) Preparation of carbon black D0
Carbon black was prepared by burning acetylene gas coming out from the reaction of water with calcium carbide. The fume product was quenched with cooled jacket water and collected in a magnetic stirrer water vessel. The primary aggregate of carbon black was respectively washed with acid, base, organic solvents (toluene, acetone), rinsed with water and baked at 140°C at least for 4 hrs in a convection oven.

2.2) Preparation of D4
The carbon black starting material D0 prepared in 2.1) was exposed to 4 times of diazo coupling process referring the previous report [1] [3]. In this case, sulfanilic acid was chosen as coupling precursor providing electrolytic group -SO\textsubscript{3}H and p-amino benzoic acid to provide –COOH. The forming of D4 product was confirmed with the significant increase of water solubility and FTIR spectroscopic measurement.

2.3) Testing procedure

i) FTIR measurement
FTIR spectroscopy measurement of LNC was carried out using FTIR Tensor 37 (Bruker) equipment.

ii) Thermal analysis
Thermal analysis of LNC was measured by DSC (Differential Scanning Calorimetry) technique using STA 409 PC-Netzsch equipment.

iii) Electrical resistivity
A pair of silver paste electrode spacing 1cm from each other was screen-printed on the top of 10mil 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. The slurry was coated on the pair of 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 the nano composite, selected aqueous emulsion polymers were added into the milling jar with suitable weight content and the test film was prepared by the same way above described.

3. RESULTS AND DISCUSSION

3.1) Electrical properties of LNC

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

Fig. 1 shows the electrical resistivity of various types of Dn products made out of D0 (in-house) using sulfanilic acid as diazo coupling agent. For a comparison purpose, Dn products were also prepared with commercial carbon black Vulcan XR 72C (Cabot Corporation). The measured data of the D1 (-COOH) product prepared with p-amino benzoic acid and in-house carbon black D0 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 D1, D4 is much higher than that of D0 in a magnification of 10\textsuperscript{3} and 10\textsuperscript{4} X, respectively, no matter what the raw carbon black material is. On the other hand, the D1(-COOH) product shows less electrical resistivity than other Dn products made out of sulfanilic acid, agreeing well with the fact that –SO\textsubscript{3}H group is known to exhibit higher protonation efficiency than the –COOH group. If we assumed that each diazo coupling cycle can add certain amount of electrolytic group to the carbon black until all of the coupling sites run out, then the electrolytic group should be the cause for the electrical conductivity reduction in the carbon black due to the increased proton transfer sites. The strong dependence of electrical resistivity on the number of diazo coupling cycle suggests that electrical resistivity can be an effective measure of the effect of coupling processes than other measurement procedures such as SEM or AFM.

3.1.2) Binder effects
As LNC product is easily and well dispersed in aqueous environment, the aqueous emulsion polymers or water soluble polymers are preferred to give a uniform dry film in which the nano scale of LNC is still maintained. However, the dried film of LNC/polymer requires the hydrophobicity to insure the performance stability with the use of liquid fuel, the aqueous emulsion polymer give better choices. In a hydrophobic solvent system, the LNC tends to reaggregate out of nano scale domain, thus hydrophobic solvent soluble polymers are not the first choice to form ideal nano composite.

Several different kinds of aqueous emulsion polymers and hydrophobic cross linking poly urethane (PU) were tested. The in-house emulsion copolymers exhibit average molecular weight in the range of 30,000- 40,000 and the T\textsubscript{g} = 100°C.

Fig. 2 exhibits the effect of binder content on the electrical resistivity of LNC (D4) for various kinds of polymer. 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:

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 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).

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 the electrical properties measured in the present study could be a mixed effect of electron transport and ionic transport properties. The detailed study of the nature of electrical transport mechanism in the nano composite will be discussed in another report. Fig. 3 is FE-SEM (Field Emission Scanning Electron Microscope, Hitachi S4800) image of the D4 LNC and the nano composite of D4 in in-house Copo3, in the scale of 500nm. It is recognized the nano scale with average size of 20-30nm of D4 in a dried stack (left). This scale is still maintained in a nano composite structure (right) in which the nano scale particles are nicely surrounded with thin layer of emulsion polymer; in-house Copo3.

Next, the binder effect on thermal properties of D4 was investigated with DTA/TG data measurement and the results are illustrated in Fig. 4. In this case, the nano composite was formulated with D4/ 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. D4 exhibits exothermic peak at 110.2°C and it could be due to the cleavage of azo bond –N=N- but the confirmation is needed in a separated study. However, it is noteworthy that this peak is completely disappeared when D4 is blended with in-house Copo3 and the mass loss of the composite film also becomes flat between 0 and 350°C. The flatness of the DTA/TG curve may reflect a recompensation in mass loss between LNC and polymeric binder and it might stabilize the azo bond against heating effect. On the other hand, the in-house Copo2 reversely, didn’t show any improvement on thermal stabilization effect but further a deterioration of thermal stability and greater mass loss. In the same Fig. 4, DTA/TG data of Nafion (from Nafion DE2201 solution) 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 100C and 450C, the mass loss in Nafion is almost completed at about 550C. 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.

Fig 5 summarizes the electrical resistivity of the nano composites, measured at various temperatures. In this case, 4 composites were formulated. These are D1, D4 blended in in-house Copol and in-house Copo3. It is observed that the nano composite comprised of D4 blended in the in-house Copol shows the highest resistivity with stable performance until 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 deterioration on the composite film.

Next, a PEM FC was formulated to test out the PEM performance of the nano composite. In this case, a PEM fuel cell structure is composed of liquid fuel diffusion layer (LDL) using Toray Carbon Paper TGPH-060 (E-Tek product) over coated with electro catalyst layer composed of 20% Pt, 10% Ru, 70% Vulcan XRF72C (E-Tek product) in anode and 30% Pt70% Vulcan XRF72C (E-Tek product) in cathode. The electro catalyst layer was prepared by mixing the electro catalysts with MEK solvent using ultrasonic bath (Branson 2510) for 5 minutes then brush painted on the LDL to achieve a weight loading of 4 mg/cm² after being baked at 80°C in a convection oven set at 80°C for 30 minutes. The active electrode area is about 4 cm². The membrane is composed of 50% D4 embedded in 50% in-house Copo3 was 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°C. The PEM thickness was detected to be around 168 um and is equivalent to that of the Nafion 117 membrane. Actually, Fig. 6 shows the V-I characteristic curves of the PEM made out of D4/Copo3 composite compared to commercial Nafion 117 product when an aqueous fuel containing 3% methanol was fed. One can recognize that the nano composite PEM shows higher current density than that of Nafion 117. Fig.7 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.

5. CONCLUSION

It can be concluded that
a) the electrolytic groups –SO3H, -COOH strongly reduce the electron conductivity of the carbon black, and enhance the proton transport properties
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 nano composite also exhibits superior heat stability over the Nafion 117 as this PEM starts deteriorated at 80°C
e) The nano composite PEM exhibits a shelf life exceeding 3.5 months with continuous feeding of aqueous methanol fuel source.

5. REFERENCES

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