

MEMBRANE ELECTRODE ASSEMBLY AND METHOD OF FORMING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application makes reference to and claims the benefit of priority of an application for “Low Cost and Large Area Growth of Vertically Aligned Carbon Nanotubes” filed on April 08, 2009 with the United States Patent and Trademark Office, and there duly assigned serial number 61/167,293. The contents of said application filed on April 7, 2009 is incorporated herein by reference for all purposes, including an incorporation of any element or part of the description, claims or drawings not contained herein and referred to in Rule 20.5(a) of the PCT, pursuant to Rule 4.18 of the PCT.

FIELD OF THE INVENTION

[0002] The present invention relates to a membrane electrode assembly as well as to a method of forming a membrane electrode assembly.

BACKGROUND OF THE INVENTION

[0003] Polymer electrolyte membrane fuel cells (PEMFCs), also known as proton exchange membrane fuel cells, are one of the most promising power sources for the future. The heart of a PEMFC is a membrane electrode assembly (MEA), which consists of two gas diffusion layers and two catalyst layers that sandwich the polymer electrolyte membrane in the middle (see Fig. 1).

[0004] Two methods are currently employed in preparing membrane electrode assemblies. One method disclosed in US patent No. 5,211,984 applies the Pt/C catalyst and a polytetrafluoroethylene (PTFE) mixture ink onto the diffusion layer. In this application PTFE serves as binder and provides the hydrophobic pathways for the diffusion of reactants to the reaction sites, preventing them from flooding. Ionomer solution is then impregnated or sprayed on the electrode to extend the proton conduction pathways and to increase the three-phase reaction sites. This PTFE-bound electrode has the advantage of good reactant mass transportation. However, its catalyst utilization is low with a value of only about 10~20%, since Pt catalysts covered by PTFE would lose their electrochemical activity.

[0005] In US patent No. 5,211,984 a further method is employed to prepare a membrane electrode assembly. The hydrophobic PTFE is replaced by a hydrophilic perfluorosulfonate ionomer (Nafion) in the Pt/C mixture ink, and the Pt/C catalyst layer is applied onto the membrane, rather than onto the gas diffusion layer. This thin-film electrode method enhances

the contact of the catalyst with the membrane, which improves not only the catalyst utilization but also the integrity of the catalyst layer/membrane interface. However, since the electrode has no hydrophobic materials to construct reactant transport channels, serious mass transport problem readily occurs, especially when air is used as the oxidant.

5 [0006] Generally, both the above two methods of preparing the MEA are unable to achieve high utilization of Pt. The Pt loading (around $0.3\text{mg}/\text{cm}^2$) of the electrodes is too high to satisfy the requirement for the commercialization of PEMFCs. Pt is expensive. According to DOE's 2006 PEMFC massive-production cost analysis, Pt counts for about 38% of the fuel cell system cost.

10 [0007] Carbon nanotubes as the support for Pt catalysts in PEMFCs have attracted great interest due to their high surface area, excellent electronic conductivity, and high chemical stability. Pt catalysts supported on carbon nanotubes (CNTs) have shown better performance in PEMFCs than those supported on conventional carbon material such as carbon black. Nevertheless the catalyst utilization for the Pt/CNTs MEA is still low.

15 [0008] US patent application 2004/0224217 discloses an integrated MEA for PEMFCs, using a free-standing axially aligned CNTs film as a catalyst support. The CNTs are prepared by CVD using anodized alumina template prior to the deposition of Pt nanoparticles within the CNTs to form a continuous axially aligned active film. The anodized aluminium template is removed using HF. US patent application No. 2004/0167014 describes a method of preparing a
20 MEA with aligned carbon nanotubes grown on conductive and porous substrates, such as carbon paper and low resistivity porous silicon. CNTs are grown by catalytic chemical vapour deposition. Pt nanoparticles are deposited on the aligned carbon nanotubes using electrochemical deposition. The removal of the template is achieved with HF or NaOH solution. US patent application No. 2006/0269827 discloses a template-free method of
25 synthesizing VACNTs for MEA fabrication. A thin quartz plate is used as a substrate for growing the VACNTs.

 [0009] The methods of the art share the problem of not being suitable for commercialization due to the requirements of an expensive substrate and a complex template removal process. It is therefore an object of the present invention to provide a method of
30 forming a membrane electrode assembly that avoids these drawbacks or shortcomings of the current techniques.

SUMMARY OF THE INVENTION

[0010] In a first aspect the present invention provides a membrane electrode assembly.

The membrane electrode assembly includes alternating layers of vertically aligned carbon nanotubes and ionomer membrane. The membrane electrode assembly includes two or more layers of vertically aligned carbon nanotubes. The vertically aligned carbon nanotubes have nanoparticles immobilized thereon. These nanoparticles include platinum.

5 **[0011]** In a second aspect the present invention provides a method of forming a membrane electrode assembly. The method includes providing aluminium foil. The aluminium foil has an upper face and a lower face. The method also includes allowing a plurality of vertically aligned carbon nanotubes to grow on the upper face of the aluminium foil. Further, the method includes depositing nano-particles on the plurality of vertically aligned carbon nanotubes
10 grown on the upper face of the aluminium foil. The method also includes depositing a plurality of ionomer molecules on the plurality of vertically aligned carbon nanotubes, which have nanoparticles deposited thereon. Further, the method includes providing an ionomer membrane. The ionomer membrane has an upper face and a lower face. The method also includes immobilizing the ionomer membrane on the vertically aligned carbon nanotubes. The
15 ionomer membrane is immobilized on the vertically aligned carbon nanotubes by means of hot-pressing. The ionomer membrane is immobilized with its upper face on a first portion of the plurality of vertically aligned carbon nanotubes that are grown on a first portion of the upper face of the aluminium foil. The ionomer membrane is immobilized with its lower face on a second portion of the plurality of vertically aligned carbon nanotubes that are grown on a
20 second portion of the upper face of the aluminium foil. By immobilizing the ionomer membrane by means of hot-pressing, the vertically aligned carbon nanotubes are transferred from the aluminium foil to the ionomer membrane. Vertically aligned carbon nanotubes are thereby transferred from the first portion of the upper face of the aluminium foil to the upper face of the ionomer membrane. Vertically aligned carbon nanotubes are also transferred from
25 the second portion of the upper face of the aluminium foil to the lower face of the ionomer membrane.

[0012] In a third aspect the invention provides a polymer electrode membrane fuel cell electrode. The polymer electrode membrane fuel cell electrode includes a membrane electrode assembly according to the first aspect.

30 **[0013]** In a third aspect the invention provides a polymer electrode membrane fuel cell. The polymer electrode membrane fuel cell includes the polymer electrode membrane fuel cell electrode according to the third aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0015] **Figure 1A** shows a membrane electrode assembly of a standard PEMFC (11: gas diffusion backings, 12: graphite block; 13: Teflon mask; 14: membrane with catalyst).

[0016] **Figure 1B** depicts aluminium foil of 3 x 6 cm with a catalyst layer immobilized thereon by spray coating.

[0017] **Figure 2** is a schematic illustration of the growth of vertically aligned carbon nanotubes on aluminium foil, the Pt deposition, and the fabrication of the MEA according to the invention. (A) spraying of a catalyst precursor onto aluminium foil, (B) the aluminium foil with the catalyst precursor immobilized thereon, (C) sintering at 500 °C, thereby forming catalyst particles, (D) growth of vertically aligned carbon nanotubes by PECVD, (E) deposition of Pt nanoparticles by means of a sputtering system, (F) impregnation of Nafion ionomers onto the film of vertically aligned carbon nanotubes (by means of a microsyringe; typically 10 µl of 0.5wt% Nafion in isopropanol was added dropwise onto the CNT film and dried at room temperature), (G) transfer of vertically aligned carbon nanotubes to the Nafion membrane by hot-pressing, (H) assembly of the MEA by sandwiching the Nafion membrane between two gas diffusion layers for single cell testing.

[0018] **Figure 3** depicts scanning electron microscopy (SEM, A, B) and transmission electron microscopy images (TEM, C, D) of vertically aligned carbon nanotubes with Pt-nanoparticles (3nm, 30 µg/cm²) distributed thereon by DC Ion Sputtering.

[0019] **Figure 4** depicts the transfer of vertically aligned carbon nanotubes on the macroscopic scale (upper panel) and on the scale depicted by scanning electron microscopy (lower panel).

[0020] **Figure 5** shows a comparison of the single cell performance at 80 °C between a Pt/VACNT electrode and a conventional electrode prepared using a commercial Pt/C catalyst from Johnson Matthey as the cathode with indicated Pt loadings.

[0021] **Figure 6** shows a comparison of an electrode according to the invention which has a low Pt loading of 35µg/cm² and good Pt distribution (20µg/cm² deposited on front side, 15µg/cm² on backside of the vertically aligned carbon nanotubes by ion sputtering) and a commercial Johnson Matthey catalyst with the indicated Pt loadings.

[0022] **Figure 7** shows comparison of an electrode according to the invention with a low

Pt loading of $35\mu\text{g}/\text{cm}^2$ Pt (2) and with a commercial ETEK catalyst with a Pt loading of $400\mu\text{g}/\text{cm}^2$ (1).

[0023] Figure 8 depicts cyclic voltammograms measured at a scan rate of 50 mV/s at room temperature in 0.5 M H_2SO_4 of vertically aligned carbon nanotubes (multi-walled carbon nanotubes, 1) and commercial multi-walled carbon nanotubes (< 10 nm, 2). Vertically aligned carbon nanotubes showed an average capacitance of 56.7 F/g, commercial multi-walled carbon nanotubes < 10 nm of 33.15 F/g.

[0024] Figure 9 depicts the selective growth of multi-walled carbon nanotubes. Fig. 9A is an SEM image of vertically aligned MWCNT. Fig. 9B depicts the Raman signal for MWCNT.

[0025] Figure 10 depicts the selective growth of single-walled carbon nanotubes. Fig. 10A is an SEM image of vertically aligned SWCNT. Fig. 10B depicts the Raman signal for SWCNT.

[0026] Figure 11 depicts the potential dependant specific capacitance of vertically aligned carbon nanotubes (multi-walled carbon nanotubes, 1) and commercial multi-walled carbon nanotubes (< 10 nm, 2) measured at a scan rate of 50 mV/s at room temperature in 0.5 M H_2SO_4 .

[0027] Figure 12 depicts cyclic voltammograms of vertically aligned single wall carbon nanotubes at scan rates ranging from 10 mV/s to 400 mV/s.

[0028] Figure 13 depicts the specific capacitance of vertically aligned single wall carbon nanotubes at scan rates ranging from 10 mV/s to 400 mV/s.

DETAILED DESCRIPTION OF THE INVENTION

[0029] This invention discloses a method of preparing low cost and large area of vertically aligned carbon nanotubes (VACNTs), in which cheap household aluminium foil is used as substrate, and spraying coating replaces expensive e-beam or ion-sputtering in depositing Co/Fe catalysts on Al. The spraying coating can evenly distribute Co/Fe catalyst on large area Al foil, while plasma enhanced chemical vapour deposition can take place on the Co/Fe catalysts at 500 °C, lower than conventional 700-900 °C. The VACNTs/Al can be used for supercapacitor electrodes. By depositing a Pt thin layer on VACNTs/Al and subsequent hot pressing, Pt/VACNTs can be 100% transferred from Al foil onto polymer electrolyte membrane for the fabrication of a membrane electrode assembly (MEA). The polymer electrolyte membrane fuel cell with the MEA fabricated by this method shows an excellent performance with super low Pt loading. In one illustrative example $0.71\text{ W}/\text{cm}^2$ of output

energy density was measured on a PEMFC of the invention with only $30\mu\text{g}/\text{cm}^2$ Pt loading. Accordingly, compared to commercial $0.42\text{ W}/\text{cm}^2$ with $50\mu\text{g}/\text{cm}^2$, Pt loading can be reduced by 2-3 times to achieve a similar performance.

[0030] The present invention provides a membrane electrode assembly, which is suitable for use in a fuel cell. Fuel cells based on polymer electrolyte membranes / proton exchange membranes are currently thought to represent the most promising devices available for high-power consumer applications, including for use in vehicles. Hydrogen fuel and oxygen from the air are used for electricity generation. In a PEM fuel cell a barrier is provided that makes use of the strong tendency of electrons to transfer from hydrogen to oxygen. Upon direct contact between hydrogen and oxygen such transfer of electrons between the two gases leads to a charge imbalance, causing ionic attraction with the consequence of bond formation between hydrogen and oxygen. Thereby heat energy is released and water formed. In a PEM fuel cell the PEM membrane separates the anode and the cathode, and electrons and protons of hydrogen are forced to flow along separate paths. The PEM membrane only allows the passage of positively charged ions, whereas electrons have to flow through an electric circuit. If the latter is removed, the fuel cell is inactive.

[0031] In a membrane electrode assembly according to the invention a plurality of vertically aligned carbon nanotubes and an ionomer membrane are provided in the form of alternating layers. The ionomer membrane prevents both hydrogen and oxygen/air to pass. The ionomer membrane is capable of conducting protons, but not electrons. The membrane is further of a material that is resistant to the reducing conditions in the area of the cathode as well as strong oxidative conditions in the area of the anode. The membrane may include a perfluorosulfonic acid membrane such as the commercially available Nafion® or a suitable non-fluorinated hydrocarbon-based polymer as for example reviewed by Rozière and Jones (Annu. Rev. Mater. Res, 2003, 33, 503-555). Examples of a respective non-fluorinated polymer include, but are not limited to sulfonated polyarylenes, polybenzimidazoles doped with a proton acid such as hydrochloric acid, phosphoric acid, perchloric acid, sulphuric acid or nitric acid, sulfonated poly(phenylquinoxalines), sulfonated poly(phenylene oxides), sulfonated poly(phenylene sulfides), poly(arylene ether sulfones), sulfonated poly(aryl ether ketones) and sulfonated polyphosphazenes.

[0032] Nanotubes are hollow in contrast to nanowires, which are solid. A carbon nanotube may be of any length and diameter. In some embodiments it may have a diameter of about 1 - 500 nm, such as about 3 - 200 nm or about 10 - 100 nm. A carbon nanotube is a cylinder of rolled up graphitic sheets. Both single- and multi-walled carbon nanotubes are known and can

equally be used in the method of the present invention. The carbon nanotubes may be of any desired length, such as in the range from about 10 nm to about 10 μm .

[0033] A nanotube of the plurality of vertically aligned carbon nanotubes may have a single wall or multiple walls. A carbon nanotube may also have one or more fullerenes covalently bonded to an outer sidewall thereof, in which case it is generally called a nanobud. A respective carbon nanotube is typically metallic, albeit nanotubes may be included that are a semiconductor or an insulator. Depending on the arrangement of the carbon hexagon rings along the surface of the nanotubes, carbon nanotubes are generally either metallic or semiconducting. The plurality of vertically aligned carbon nanotubes accordingly includes, and in one embodiment is, a plurality of electrically conductive nanofilaments. A membrane electrode assembly of the invention includes an ionomer membrane with an upper face (or a first face) and a lower face (or a second face). A plurality of vertically aligned carbon nanotubes is arranged on either side of the ionomer membrane, i.e. on both the upper face and the lower face. Such an arrangement has previously not been described for vertically aligned carbon nanotubes. International patent application WO 2006/099593 discloses a proton exchange membrane for fuel cells with aligned carbon material on one side and carbon black on the other side. Carbon nanotubes have a particularly high surface area, excellent electronic conductivity, and high chemical stability (*supra*). Vertically aligned carbon nanotubes (VACNTs) are thought to have even better electronic conductivity and mass transportation capacity than randomly orientated carbon nanotubes, since electronic conduction along the CNT axis is better and the stacking of randomly orientated carbon nanotubes increases the difficulty for reactant diffusion.

[0034] The carbon nanotubes may be without any functional groups or have some or many functional groups of any desired type. Typically the carbon nanotubes included in a membrane electrode assembly of the invention are at least essentially without functional groups or poorly functionalized. The term "functionalizing" generally refers to the introduction of functional groups to the carbon material. Any functional group may be introduced into the carbon material. Typical functional groups introduced by the method of the invention include, but are not limited to, -COOH (carboxy), -CHO (aldehyde), -CO- (carbonyl), -OSO₃H (sulfate), -OSO- (sulfonyl), -O- (oxo) and -OH (hydroxy). Other functional groups, which may already be present in the carbon material, or in some embodiments be generated during the method of the invention, include for example -NH₂ (amino), -NO (nitro), -Br (bromo), -Cl (chloro) and -F (fluoro). It is noted that some functional groups such as a -Cl group, may in some cases act as a poison for a metal catalyst, and may thus affect the function of a fuel cell. If a certain functionalization is desired, optimization and careful testing may therefore be required.

[0035] As the plurality of vertically aligned carbon nanotubes immobilized on the upper side of the membrane can be taken to define a first vertically aligned plurality of electrically conductive nanofilaments and the vertically aligned carbon nanotubes on the lower side can be taken to define a second vertically aligned plurality of electrically conductive nanofilaments, the membrane electrode assembly can also be taken to involve a first plurality of electrically conductive nanofilaments (carbon nanotubes) on a first (upper) side and a second plurality of electrically conductive nanofilaments on a second (lower) side of the membrane.

[0036] On the vertically aligned carbon nanotubes that are included in the membrane electrode assembly according to the invention there are nanoparticles immobilized. These nanoparticles include platinum. They may also include a further metal that can act as a catalyst in a fuel cell, such as rhutenium or gold. The nanoparticles may be of any desired shape, such as for example spherical. In some embodiments the nanoparticle may be of non-homogenous structure. As an illustrative example, the nanoparticle may have a core that includes further matter such as a metal that differs from platinum, rhutenium and gold. The nanoparticles have a maximal width, e.g. a diameter, below 1 μm . They may in some embodiments have a maximal width of less than about 100 nm, such as less than about 50 nm, less than about 30 nm, less than about 15 nm or less than about 10 nm, such as about 1 nm or less, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm or about 10 nm.

[0037] A membrane electrode assembly according to the present invention is formed by means of aluminium foil. The aluminium foil is used as a low-cost and safe means for forming a plurality of vertically aligned carbon nanotubes and for transferring them to both sides of a polymer electrolyte membrane. The aluminium foil may be provided in any desired form such as one or more sheets. It may for example have a thickness in the range of several microns, e.g. about 4 μm to about 300 μm , which is the range in which typical conventional household aluminium foil is available. Illustrative examples of embodiments of commercial available aluminium foil that may be used are foil with a thickness of 6 μm , 12 μm , 14 μm , 15 μm , 20 μm or 90 μm . Any household aluminium foil may be used. It has previously been shown that vertically aligned carbon nanotubes can be formed on aluminium foil (Yoshikawa, N, et al., Nanotechnology (2008, 19, doi:10.1088/0957-4484/19/24/245607). The present inventors have found that this approach is well suited and particularly useful for the transfer of the obtained vertically aligned carbon nanotubes to a polymer electrolyte membrane. The conventional silicon substrate is expensive. Furthermore, vertically aligned carbon nanotubes grown on silicon wafer or quartz are difficult to transfer by hot-press since the substrates are brittle. Their debris can be a hazard of piercing the polymer membrane, resulting in the crossover and

direct combustion of the reactant gases. In contrast thereto vertically aligned carbon nanotubes grown on aluminium foil can be easily and completely transferred to a polymer membrane by hot-press due to the weak interactions between the carbon nanotubes and the aluminium foil. Furthermore, aluminium foil is very flexible and has good mechanical strength. It can be easily cut into any desired dimensions and any shapes.

[0038] Aluminium foil used has an upper face and a lower face, which may also be taken to be a first and a second face. In embodiments where several portions, such as several sheets of aluminium foil are used, each of the respective portions may then have such an upper face and such a lower face. For convenience the aluminium foil may be arranged on an at least essentially straight and plane surface. The lower face then faces the respective surface on which the aluminium foil is arranged and the upper face can be used to immobilize or grow vertically aligned carbon nanotubes thereon. In order to grow carbon nanotubes on the aluminium foil, catalyst particles are typically deposited on the upper face of the aluminium foil. The catalyst particles may include one or more transition metals of Group VIII of the Periodic Table of the Elements according to the old IUPAC system, which corresponds to groups 8-10 of the Periodic Table of the Elements according to the current IUPAC system. Illustrative examples of respective elements are Fe, Co, Ru, Ni, Pt, Pd or Rh.

[0039] These catalyst particles may in some embodiments be derived from a precursor. The precursor may be a compound of the one or more transition metals of Group VIII of the Periodic Table of the Elements (supra). These compound(s) may for instance be one or more organic compounds such as salts of a carboxylic acid. Any carboxylic acid may be used. The carboxylic acid may be of any desired length, include any desired number of heteroatoms and functional groups. In some embodiments the carboxylic acid is a hydroxy carboxylic acid, a dicarboxylic acid (including a tricarboxylic acid), an amino acid or any mixture thereof. To provide a number of illustrative examples, the organic carboxylic acid may be oxalic acid, ascorbic acid, citric acid, glycolic acid, tartaric acid, malic acid, maleic acid, adipic acid, lactic acid, salicylic acid or any mixture thereof. Examples of a suitable amino acid include, but are not limited to, glutamine, lysine, histidine, serine, threonine, tyrosine, cystine, cysteine, arginine, proline, glutamic acid, aspartic acid, asparagine, glutamine or any mixture thereof. The carboxylic acid may be solid or liquid and it may also be provided in form of a solution or dispersion. Any liquid may be used in this regard. In some embodiments the catalyst precursor may be deposited on the aluminium foil. Subsequently the aluminium foil may be exposed to elevated temperature, e.g. be sintered with the catalyst precursor deposited thereon. The elevated temperature may be selected between ambient temperature and the melting point of aluminium, i.e. between about 25 °C and 660 °C, such as in the range from about 100 °C to

about 660 °C, about 200 °C to about 650 °C, about 250 °C to about 650 °C, about 300 °C to about 650 °C, about 350 °C to about 650 °C, about 400 °C to about 650 °C, about 400 °C to about 620 °C, about 450 °C to about 600 °C or about 450 °C to about 550 °C, such as e.g. 500 °C.

5 **[0040]** The catalyst precursor may be deposited on the aluminium foil by spray-coating. The catalyst precursor may be provided in a suitable solvent. Where a carboxylic acid salt is used a polar solvent, in particular a polar protic solvent may be used. Examples of polar protic solvents include, but are not limited to, water, methanol, ethanol, propanol, isopropanol, butyl alcohol, formic acid, dimethylarsinic acid $[(\text{CH}_3)_2\text{AsO}(\text{OH})]$, N,N-dimethyl-formamide, N,N-diisopropylethylamine, or chlorophenol. Compared to E-beam and RF sputtering deposition
10 technologies, spray coating technology may be taken to be advantageous since it is simple, cheap and rapid. Compared to dip coating or spin coating, spray coating has the advantage of preparing the catalyst layer evenly also on large-area aluminum foil (e.g. > 3x6 cm in the photo depicted in Fig. 1B). Most importantly, the catalyst density can be controlled easily by spray
15 coating, when compared to other coating technologies. Thereby the carbon nanotubes density in a VACNT film can be conveniently be controlled. This is significantly important as it facilitates the subsequent deposition of nanoparticles that include Pt on the vertically aligned carbon nanotubes. Easy control of the density of the carbon nanotubes facilitates the mass transportation for PEMFCs. The porous structure is a critical issue for the successful
20 application of PEMFCs. During operation of a fuel cell, the gas mixture is delivered from the cathode towards the nanoparticles that include Pt, i.e. the catalyst of the fuel cell, by convention through the gas diffusion layer, so that accessibility of the nanoparticles is an important factor for the performance of the respective fuel cell.

25 **[0041]** Growing the plurality of vertically aligned carbon nanotubes may be carried out by means of applying plasma enhanced chemical vapour deposition using a suitable carbon source. The carbon source may be provided in any form, such as in form of a gas, a powder, an aerogel (e.g. of carbon nanotubes (for an indication on the handling of a respective aerogel see e.g. Bryning, M.B., et al., *Advanced Materials* (2007) 19, 661-664)), one or more solid blocks, a suspension, a dispersion or a solution. Where a solution, suspension or dispersion is
30 provided, a liquid such as a commercially available solvent or water is used. Any desired liquid can be employed, whether an aqueous or non aqueous liquid, an organic liquid (solvent), or a nonpolar aprotic, nonpolar protic, dipolar protic, dipolar aprotic, or an ionic liquid. Examples of nonpolar aprotic liquids include, but are not limited to, hexane, heptane, cyclohexane, benzene, toluene, pyridine, dichloromethane, chloroform, carbon tetrachloride,
35 carbon disulfide, tetrahydrofuran, dioxane, diethyl ether, diisopropylether, ethylene glycol

monobutyl ether or tetrahydrofuran. Examples of dipolar aprotic liquids are methyl ethyl ketone, methyl isobutyl ketone, acetone, cyclohexanone, ethyl acetate, isobutyl isobutyrate, ethylene glycol diacetate, dimethylformamide, acetonitrile, N,N-dimethyl acetamide, nitromethane, acetonitrile, N-methylpyrrolidone, and dimethylsulfoxide. Examples of nonpolar protic liquids are acetic acid, tert.-butyl alcohol, phenol, cyclohexanol, or aniline. Two illustrative examples of ionic liquids are 1,3-dialkylimidazolium-tetrafluoroborates and 1,3-dialkylimidazolium-hexafluoroborates. Three illustrative examples of a carbon source in the gas phase are acetylene, ethylene and methane. The temperature at which the plasma enhanced chemical vapour deposition is carried out may be selected between about 350 °C and the melting point of aluminium, i.e. 660 °C, such as in the range from about 400 °C to about 660 °C, about 450 °C to about 650 °C, about 450 °C to about 600 °C, about 450 °C to about 550 °C or about 400 °C to about 550 °C, such as e.g. 500 °C. A suitable example of carrying out plasma enhanced chemical vapour deposition to obtain vertically aligned carbon nanotubes has been disclosed by the present inventors (Luo et al., Nanotechnology (2008) 19, doi: 10.1088/0957-4484/19/25/255607, incorporated herein by reference in its entirety).

[0042] In a process according to the present invention nanoparticles (cf. above) are deposited onto the plurality of vertically aligned carbon nanotubes that are grown on the upper face of the aluminium foil. Such nanoparticles may be deposited by any suitable method, such as a physical method. In one embodiment DC ion sputtering is used. Thereby super low particle loading can be achieved. As an example, in the photos depicted in Fig. 3 vertically aligned carbon nanotubes with platinum particles at a Pt loading of 30 µg/cm² are shown, obtained using ion sputtering. Where desired nanoparticles, may also be driven into the carbon nanotubes, for example via decomposition of precursors or via impregnation as described by Castillejos et al. (Angew. Chem. Int. Ed. (2009) 48, 2529-2533). Other methods that may be applied for depositing Pt to vertically aligned CNTs, include, but are not limited to, RF ion sputtering, E-beam evaporation, pulsed laser deposition, atomic layer deposition and chemical impregnation.

[0043] Molecules of an ionomer are deposited on the plurality of vertically aligned carbon nanotubes with nanoparticles deposited thereon. This deposition may be carried out by impregnation, e.g. wetness impregnation using a solution of the ionomer compound. The ionomer used is suitable for supporting hot-pressing of the ionomer membrane, which is a membrane of a polymer that includes the ionomer molecules, in order to immobilize the vertically aligned carbon nanotubes onto the ionomer membrane. The ionomer molecules typically have properties in terms of polarity and reactivity that match the corresponding properties of the material of the ionomer membrane to support a respective immobilization. In

some embodiments the ionomer of the ionomer molecules used is identical to the ionomer material of the ionomer membrane. In typical embodiments the ionomer molecules that are deposited onto the vertically aligned carbon nanotubes are molecules of the same ionomer that is included in the ionomer membrane. In some embodiments the ionomer membrane includes, including consists of, a single type of ionomer. The term "ionomer membrane" as used herein, refers to a polymer that includes, including consists of, monomers that correspond to ionomer molecules. The ionomer membrane consists of a polymer, which may be formed from ionomer molecules. Typically, these ionomer molecules are of the same chemical structure as the ionomer molecules used for deposition onto the plurality of vertically aligned carbon nanotubes. It is understood that the ionomer molecules and the polymer of the ionomer membrane may be provided in ionic form. In such embodiments different counter ions such as Na^+ or TBA^+ may be used. The ionomer molecules deposited onto the vertically aligned carbon nanotubes act as a binder and integrate the catalyst layer and the polymer membrane.

[0044] An ionomer membrane is then provided. The ionomer membrane is of an ionomer material as defined above, with an upper face (or a first face) and a lower face (or a second face). Both the upper face and the lower face of the ionomer membrane, are used for immobilization of vertically aligned carbon nanotubes. Immobilizing is carried out by means of hot-pressing. For this purpose the ionomer membrane is arranged on a first portion of the plurality of vertically aligned carbon nanotubes grown on a first portion of the upper face of the aluminium foil with its upper face. As an illustrative example the ionomer membrane may be of dimensions in the plane of the upper face of the aluminium foil that are smaller than the dimensions of aluminium foil with vertically aligned carbon nanotubes grown thereon. If the entire ionomer membrane is to be used for transfer of carbon nanotubes onto the same it will accordingly be of dimensions that allow both sides of the ionomer membrane to be positioned onto different portions of the aluminium foil. The dimensions of the ionomer membrane may for example be at least half of the dimensions of the aluminium foil. As a further illustrative example the aluminium foil may be provided in the form of several separate portions. Several portions may for example have been used for growing vertically aligned carbon nanotubes thereon. Several portions may for example also have been obtained by cutting aluminium foil after growing vertically aligned carbon nanotubes thereon.

[0045] The ionomer membrane is further arranged on a second portion of the plurality of vertically aligned carbon nanotubes grown on a second portion of the upper face of the aluminium foil with its lower face. The aluminium foil may for instance be bent in such a way that a first portion thereof is in contact with the first portion of the ionomer membrane and a second portion thereof is in contact with the second portion of the ionomer membrane. The

aluminium foil may thereby be wrapped around the ionomer membrane. The aluminium foil may also be provided in the form of several separate parts of aluminium foil. Similar to embodiments where a single aluminium foil is provided, two portions of aluminium foil may then be arranged on opposite sides of the ionomer membrane. A first part, defining the first portion of aluminium foil may be brought in contact with the first portion of the ionomer membrane may be arranged on the first side and a second part, defining the second portion of aluminium foil may be arranged on the second side of the ionomer membrane. The respective surfaces of aluminium foil and ionomer membrane are brought in contact with each other and hot-pressed.

[0046] The ionomer membrane with the vertically aligned carbon nanotubes immobilized thereon may then be sandwiched between two gas diffusion layers. Any conventional gas diffusion layer may be used, which is typically of a non-polar material such as polytetrafluoroethylene. This diffusion layer serves inter alia in controlled the content of the formed water around the platinum containing nanoparticles, which define the catalyst of the electrode membrane fuel cell

[0047] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

EXEMPLARY EMBODIMENTS OF THE INVENTION

[0048] A schematic illustration of the growth of VACNTs on aluminum foil and the fabrication of MEA is shown in Fig. 2. The details on the method are as follows.

Step1- deposition of catalyst on Al foil

[0049] A piece of Al foil (7cm (width) × 13cm (length) × 15μm (thickness) cleaned by acetone was fixed on a stainless steel plate. Ethanol solution containing 6ml×7mM of iron acetate and cobalt acetate was evenly sprayed on the surface of Al foil followed by heating treatment at 500 °C for 10min in air to synthesize the FeCo bimetallic catalyst for the growth of VACNTs. This procedure was repeated for several times to reach the desired density of catalyst nanoparticles on the Al foil.

Step 2- growth of VACNTs by PECVD:

[0050] The catalyst-loaded Al foil was then positioned into the chamber of a radio frequency (13.56 MHz) plasma-enhanced chemical vapor deposition (PECVD) system. The sample chamber was evacuated to a pressure of $\sim 10^{-5}$ Pa using a turbo pump in conjunction with a rough vacuum pump to remove the atmospheric impurities. 20 sccm of H₂ gas was

supplied into the chamber and the pressure was adjusted to 133 ± 5 Pa (i.e. ~ 1 Torr). The temperature of the graphite heater was ramped from the initial temperature to 500°C at a rate of $100^\circ\text{C}/\text{min}$. Once the final temperature was reached, the radio frequency power (30 W) was switch on to activate the hydrogen plasma to etch the FeCo bimetallic catalyst for 2 min. Subsequently, 20 sccm: 40 sccm of $\text{H}_2 : \text{C}_2\text{H}_2$ was introduced into the chamber and the growth time was 20 min.

Step3- Pt nanoparticles deposition on VACNT film

[0051] Pt nanoparticles on a vertically aligned carbon nanotubes (Pt/VACNT) film were prepared by the DC and RF sputtering method. For the DC sputtering, the deposition time was 30s and the sputter current was set at 20mA. The procedure was repeated several times to achieve a desired Pt loading on VACNTs.

[0052] RF sputtering process was performed with a radio frequency magnetron sputtering system (Denton Discovery-18). A 3 inch of pure Pt target (purity 99.99%) was mounted at the sputter cathode of the system. During the sputtering process, the input power for the sputter cathode was 50 W and the Ar gas pressure was 10 mTorr. To obtain a Pt loading of $20 \mu\text{g}/\text{cm}^2$, the samples were subject to the Pt plasma for a total sputtering time of 120s. For the post-transfer Pt-deposition, $15 \mu\text{g}/\text{cm}^2$ Pt was sputter-deposited via the same sputtering process for 90s.

Step4- Fabrication of MEA for PEFC

[0053] The Pt/VACNT film was cut into $2 \times 2 \text{ cm}^2$ followed by impregnation of 100 μl of Nafion ionomer ($10 \mu\text{l} \times 5\text{wt}\%$ Nafion solution in 1ml isopropanol) and it was then transferred onto the surface of a Nafion 212 membrane by hot-pressing at 130°C under $30 \text{ kg}/\text{cm}^2$ for 90 s. The platinized VACNT film was served as the catalyst layer for the cathode of polymer electrolyte fuel cell (PEFC). Anode electrode was prepared by the conventional thin film method using 40% Pt on carbon black catalyst from Johnson Matthey. Pt loading of anode is $0.4 \text{ mg}/\text{cm}^2$. Wet-proof carbon paper with a microporous layer (Toray TGPH-090) was used as the gas diffusion layer. The Pt/VACNT coated membrane was sandwiched between the anode and the gas diffusion layer, followed by hot-pressing at 130°C with a pressure of $30 \text{ kg}/\text{cm}^2$ for 1 min to form a membrane electrode assembly (MEA). For the purpose of comparison, cathode electrodes with corresponding Pt loading were prepared by the same preparation method for the anode electrodes, using 40% Pt on carbon black catalyst from Johnson Matthey.

[0054] Single cell performance and the power output of Pt/VACNT film as electrodes in

the PEFC were evaluated at 80 °C under a back pressure of 30 psi using Arbin fuel cell test station (FC-50W). The hydrogen and oxygen reactant gases were externally humidified at dew point temperature of 80 °C and 70 °C respectively. The flow rate is 400 sccm / min for both hydrogen and oxygen.

5 **High performance of our Pt/VACNTs PEM fuel cell with super low Pt loading**

[0055] Pt/VACNTs PEMFC according to the invention shows excellent performance, 0.71 W/cm² vs. 0.42 W/cm² of conventional PEMFC, even though the Pt loading on the electrode is decreased from 50 µg/cm² to 30µg/cm². This is mostly due to super high catalyst utilization, highly effective and sufficient electron, proton and reactant and products transfer pathways
10 provide by the VACNTs.

[0056] Fig. 5 compares single cell performance at 80 °C between Pt/VACNT electrode and conventional electrode prepared using commercial Pt/C catalyst from Johnson Matthey as cathode. Pt/C-JM=50µg and Pt/C-JM=100µg electrode were prepared by commercial Pt/C catalyst from Johnson Matthey with Pt loading of 50 µg and 100 µg respectively. The
15 Pt/VACNT electrode is significantly better than Pt/C-JM=50µg electrode, but slightly poorer than Pt/C-JM=100µg. The current density at 0.6V is 0.54, 0.89 and 1.07 A/cm² for Pt/C-JM=50µg, Pt/VACNT and Pt/C-JM=100µg respectively. The maximum power density of Pt on Pt/C-JM=50µg, Pt/VACNT and Pt/C-JM=100µg are 0.42, 0.71 and 0.8 W/cm² respectively. It is noteworthy that the Pt loading of Pt/VACNTs electrode is 30 µg, which is only 60% and
20 33% of the Pt loading of Pt/C-JM=50µg and Pt/C-JM=100µg electrodes, respectively.

[0057] A particular improvement can typically be achieved if the Pt coating is carried out by depositing on both sides of the vertically aligned CNT by ion sputtering. The blue curve in Fig. 6 was obtained from the new electrode which has low Pt loading (35µg/cm²) and good Pt distribution (20µg/cm² deposited on front side, 15µg/cm² on backside of the vertically aligned
25 CNT by ion sputtering). The maximum power density is 0.85 W/cm² vs 0.8 W/cm² of a commercial JM catalyst with a Pt loading of 100 µg/cm². The Pt loading of Pt/VACNTs electrode is 35 µg, which is only 35% of the Pt loading of commercial Pt/C-JM=100µg electrodes. Thus the cell with VACNTs electrode prepared using our method shows an excellent performance at a super low Pt loading. It is possible to reduce the Pt loading by 3
30 times to achieve a similar performance.

[0058] As shown in Fig. 7, the 35 µg/cm² Pt/VACNT according to the invention is comparable to commercial ETEK catalyst with a Pt loading of 400 µg/cm².

[0059] Thus the cell with VACNTs electrode prepared using the method of the invention

shows an excellent performance at a super low Pt loading. It is possible to reduce the Pt loading by 2-3 times to achieve a similar performance.

[0060] In PEMFC, the MEA performance critically depends on the area of three-phase boundaries, in which active catalyst must be accessible to protons, electrons, and reactants/products molecules in both gaseous and liquid phases. In the conventional MEA prepared by wet chemical process, catalyst layer is constructed by Pt/C powder and ionomer. Ionomer is proton conductor, not electron conductor. Ionomer in the catalyst layer can significantly decrease the proton transfer resistance, but too much ionomer will increase the resistance for electron transfer. Therefore, in order to maximize the three-phase boundary area, the content of ionomer must be carefully optimized. In our experiment, the weight ratio of Nafion to Pt/C catalyst is 1:3, which is usually used in the conventional MEA. In the conventional method, some Pt nanoparticles will be covered by ionomer and not accessible to reactant or electron conduction paths, while some might not be in contact with the ionomer. For these reasons, catalyst utilization of conventional MEA is low. In our method, VACNT film which is used as catalyst support is in close contact with both Pt particles and the proton conducting membrane at one end, while its another end is in close contact with gas diffusion layer which is current collector. Thereby the electron, proton, and gas molecules transfer pathways are integrated with Pt/VACNT catalyst layer by hot press. Pt nanoparticles become accessible and utilizable. Thus, our method can maximize the three-phase boundaries in the catalyst layer, providing super high catalyst utilization. Compared to conventional method, MEA fabricated by our method show a significantly higher performance using less catalyst.

[0061] As shown in the above cyclic voltammograms measured at a scan rate of 50 mV/s at room temperature in 0.5 M H₂SO₄, VACNTs (MWCNTs) obtained in a process according to the invention possess average capacitance 56.7 F/g, which is 1.7 times that of commercial MWCNTs<10nm. Furthermore if the VACNTs are composed of SWNTs which encapsulate linear carbon chains within their hollow core (theses SWNT were synthesized by the inventors) the capacitance can be increased to 66 F/g, almost 2 times of commercially available MWNT.

[0062] A special plastic cover was sealed over the thin film of SWNT deposited on Al substrate such that it exposed a circular area of 1.13 cm². A gold foil was also attached to the back of the Al substrate to act as the current collector. The electrochemical characteristics of SWNT electrodes were studied by cyclic voltammetry (CV) with scan rate from 10 to 100 mV/s using Autolab electrochemical unit. A three-electrode cell setup was employed for the CV measurements with Pt as the counter electrode and Ag/AgCl as the reference electrode.

The electrodes were immersed in 0.5M Na₂SO₄ electrolyte which was bubbled with argon gas to remove oxygen from the solution. The capacitance of SWNT electrodes was estimated from the CV plots in Fig 4 by integrating the area under the current density-potential plots and then dividing it by the scan rate or according to the following equation: $C = q/(\Delta V \cdot m)$, where ΔV is

the potential window from -0.25 to 0.3 V and the charge $q = \int_{-0.25}^{0.3} \frac{I(V)}{\nu} dV$ such that $I(V)$ is

the current depending on the scan rate ν , and m is the mass of nanotubes. The mass of the nanotubes, m , was estimated by subtracting the total mass of the nanotubes and Al foil (before CV measurements) with the mass of a blank Al foil (wiping away all the nanotubes from the substrate after CV measurements) using a Sartorius Microbalance ME5. To demonstrate the potential of thin film SWNT electrodes, we measured the cyclic voltammetry (CV) of SWNT electrodes using a three-electrode cell. The CV measurement is commonly used to evaluate the electrochemical performance of supercapacitor electrodes during the charging and discharging processes. Fig. 11 and Fig. 12 compare the CV plots of SWNT electrodes immersed into 0.5M Na₂SO₄ electrolyte with scan rate from 10 to 100mV/s. The CV plots of SWNT electrodes exhibit rectangular box-like electrochemical double-layer capacitor (EDLC) shapes without any faradaic reactions and reach maximum capacitances of ~67 F/g at 40mV/s.

[0063] In summary, the above examples illustrate that the method of the invention provides a method of preparing low cost and large area of VACNTs, and a method of fabricating a membrane electrode assembly (MEA) for PEMFC with high performance and low Pt loading. VACNTs/Al, which is also promising for supercapacitor applications.

[0064] The listing or discussion of a previously published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge. All documents listed are hereby incorporated herein by reference in their entirety for all purposes.

[0065] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including," "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by exemplary embodiments and optional features, modification and

variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

5 [0066] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

10 [0067] Other embodiments are within the following claims. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

What is claimed is:

- 5 1. A membrane electrode assembly comprising alternating layers of vertically aligned carbon nanotubes and ionomer membrane, wherein the membrane electrode assembly comprises two or more layers of vertically aligned carbon nanotubes and wherein the vertically aligned carbon nanotubes have nanoparticles immobilized thereon, the nanoparticles comprising platinum.
- 10 2. The membrane electrode assembly of claim 1, wherein the alternating layers of vertically aligned carbon nanotubes and ionomer membrane are obtainable by transferring the vertically aligned carbon nanotubes from aluminium foil to the ionomer membrane.
3. The membrane electrode assembly of claim 2, wherein transferring the vertically aligned carbon nanotubes to the ionomer membrane is carried out by hot-pressing of the ionomer membrane onto vertically aligned carbon nanotubes.
- 15 4. A method of forming a membrane electrode assembly, the method comprising.
 - providing aluminium foil, the aluminium foil having an upper face and a lower face,
 - allowing a plurality of vertically aligned carbon nanotubes to grow on the upper face of the aluminium foil,
 - depositing nano-particles on the plurality of vertically aligned carbon nanotubes grown on the upper face of the aluminium foil,
 - 20 - depositing a plurality of ionomer molecules on the plurality of vertically aligned carbon nanotubes with nanoparticles deposited thereon,
 - providing an ionomer membrane, wherein the ionomer membrane has an upper face and a lower face, and
 - 25 - immobilizing by means of hot-pressing the ionomer membrane with its upper face on a first portion of the plurality of vertically aligned carbon nanotubes grown on a first portion of the upper face of the aluminium foil, and with its lower face on a second portion of the plurality of vertically aligned carbon nanotubes grown on a second portion of the upper face of the aluminium foil, thereby transferring the vertically aligned carbon nanotubes from the aluminium foil to the ionomer membrane.
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5. The method of claim 4, further comprising: positioning the ionomer membrane, onto which the carbon nanotubes have been transferred, between two gas diffusion layers.
6. The method of claims 4 or 5, wherein allowing a plurality of vertically aligned carbon nanotubes to grow on the upper face comprises:
 - 5 - depositing catalyst particles on the upper face of the aluminium foil.
7. The method of claim 6, wherein depositing catalyst particles comprises depositing a catalyst precursor on the aluminium foil and subsequently sintering the aluminium foil with the catalyst precursor deposited thereon.
8. The method of claim 7, wherein the catalyst precursor comprises a Group VIII transition
10 metal compound.
9. The method of claims 7 or 8, wherein depositing a catalyst precursor on the aluminium foil is carried out by spray-coating the same on the aluminium foil.
10. The method of any of claims 4 - 9, wherein allowing a plurality of vertically aligned carbon nanotubes to grow on the upper face of the aluminium foil comprises: applying
15 plasma enhanced chemical vapour deposition using a suitable carbon source.
11. The method of claim 10, wherein the carbon source is $\text{CH}_2\text{-CH}_2$.
12. The method of any one of claims 4 - 11, wherein the first portion and the second portion of the aluminium foil are comprised in separate pieces of aluminium foil.
13. A polymer electrode membrane fuel cell electrode comprising the membrane electrode
20 assembly of one of claims 1-3.
14. A polymer electrode membrane fuel cell comprising the electrode of claim 13.