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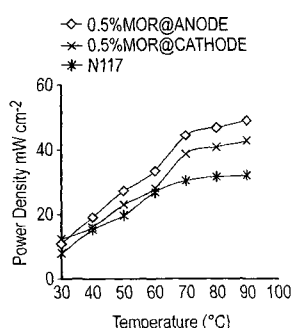


FIG. 24(a)

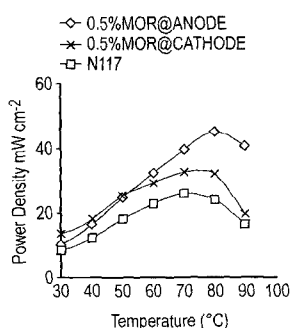


FIG. 24(b)

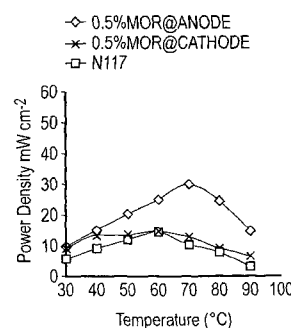


FIG. 24(c)

(57) Abstract: The present invention relates to a membrane electrode assembly, a method of making membrane electrode assemblies and direct alcohol fuel cells comprising a membrane electrode assembly of the present invention. The membrane electrode assembly of the present invention exhibits reduced alcohol crossover as compared to conventional membranes as a result of its structure.

Membrane Electrode Assembly

The present invention relates to a membrane electrode assembly, a method of making membrane electrode assemblies and direct alcohol fuel cells comprising a membrane electrode assembly of the present invention.

Proton exchange membrane (PEM) fuel cells represent one of the leading fuel cell technologies. PEM fuel cells are extremely efficient, do not produce noise, and are relatively simple to manufacture and therefore are suitable for use in a broad range of applications.

PEM fuel cells employ an ion conducting electrolyte membrane between a positive electrode and a negative electrode. The ion conducting membrane material plays a critical role in the operation of the PEM fuel cells. It acts as an ion conductor between the anode and the cathode, as a separator for the fuel and oxidant and as an insulator between the cathode and anode so that electrons conduct through an electronic circuit and not directly through the membrane.

A direct alcohol fuel cell (DAFC), e.g. a direct methanol fuel cell (DMFC), uses an alcohol as a fuel which is directly fed to the anode. A direct alcohol fuel cell has the advantage that a liquid fuel composed of an alcohol and water has the dual functionality of a coolant as well as a fuel. Direct alcohol fuel cells are compact and lightweight and can operate for long periods of time. They are also very easy to refuel.

A direct alcohol fuel cell does have drawbacks. The most significant problem of a direct alcohol fuel cell is the degradation of the cell performance due to alcohol cross-over from the anode to the cathode. There have been a number of attempts to overcome this problem which are discussed in detail below.

Alcohol, for example methanol, permeability and proton conductivity are good metrics for DMFC performance and can be used as an indication for any possible enhancement. Testing data for the actual performance of a DMFC can be obtained by the method disclosed in Li, Roberts, Holmes; Evaluation of composite membranes for DMFC; JPS; 2006; 154(1), p115-123.

US2004/0241520 discloses a method of manufacturing a composite polymer electrolyte membrane coated with an inorganic thin film, and a use of the coated membrane in a fuel cell. The invention utilises a plasma enhanced chemical vapour deposition (PECVD) method. PECVD is a very expensive process to run commercially. It is speculated in US2004/0241520 that the polymer electrolyte membrane could be coated with an inorganic film comprising a zeolite. However, the preparation of a zeolite film utilising

PECVD is not exemplified in this document. Furthermore, it is considered that it would not be possible to produce a zeolite film by employing the PECVD process.

The inorganic film exemplified in this patent application as a silica or alumina material up to 70 nm thick. It is disclosed in this document that the ionic conductivity of the composite polymer electrolyte membranes is reduced by about 20% as compared to the ionic conductivity of a bare, uncoated Nafion membrane. This is clearly disadvantageous since a high ionic conductivity is one of the most important characteristics of the membrane.

WO2004/015801 discloses a composite electrolyte for fuel cells that includes an inorganic cation exchange material, a silica-based binder and a polymer-based binder. The problem addressed by the composite electrolyte of this disclosure is to alleviate the water management problems associated with electrolyte membranes when the membranes are used at high temperatures. The types of cation exchange materials include clays, zeolites, hydroxides, and inorganic salts. The amount of inorganic cation exchange material in the composite electrolyte is disclosed as being about 10 wt % to about 99 wt %. However, this level of cation exchange material reduces the power density of the fuel cell to below a workable level. In fact, it is disclosed in WO2004/015801 that the current density of these membranes when incorporated into an MEA (which is related to the power density by the equation: power density = voltage x current density) at ambient temperature, for hydrogen and air is only 5 mA/cm². Referring to US2004/0241520, any membrane that affects the proton conductivity by -20% will negatively affect fuel cell performance.

It should be noted that it is not possible to compare two different fuel cell systems unless they are benchmarked. Better (or worse) power densities can be achieved by changing the cell configuration and catalyst loading. Hence it is usual to benchmark cells during testing for comparative purposes. A direct comparison of the fuel cell of US2004/0241520 and WO2004/015801 is therefore very difficult because the fuel cells have not been benchmarked against a standard fuel cell (i.e. a Nafion 117 fuel cell) using methanol as fuel.

The actual current densities achieved by the MEA within the DMFC systems of the present invention ranged from 125-300 mAcm⁻² for the temperature range 30-90°C in comparison to the standard current densities (i.e. current densities resulting from MEAs having no zeolite loading) which ranged from 100-250 mAcm⁻² over the same temperature range. Surprisingly, the current density value for the fuel cell of the invention is far in excess of the current density of 5mAcm⁻² obtained in WO2004/015801. Additionally, it is noteworthy that the membrane of the invention yielded maximum power densities in excess of 50mWcm⁻² in comparison to ~32mWcm⁻² obtained for the standard Nafion cell.

WO2009/073055 discloses a multilayered membrane including alternating layers of hydrophilic, nano-sized particles and recast perfluorosulfonic acid (PFSA) proton conductors. This document aims to provide a membrane having a continuous internal hydration at the anode during operation by using water generated at the cathode. It is disclosed that the particle concentration in each layer is high in order to improve the mechanical strength of the hybrid multilayer film. Such a high concentration of particles is likely to reduce the power density of the MEA. The concentration of the nanoparticles in one of the layers containing the nanoparticles based on the dry weight of the conductive electrolyte polymer in that layer ranges from 0.1 to 100%. This document discloses that low level loading of the nanoparticles (i.e. loading at 3 – 10%) into the membrane does little to enhance the conductivity of the membrane. In contrast, high level loading of the nanoparticles (i.e. loading at 30%) into the membrane does enhance the conductivity of the membrane but has the disadvantage that the membrane is very brittle and unusable. To overcome the problem of the brittleness of the membranes having high loading of the nanoparticle, this document suggests providing the complicated multilayered arrangement.

US2010/0038316 discloses a poly(tetrafluoroethylene) (PTFE) zeolite composite useful in processes such as filtration and separation. The composite comprises from 1 to 20% zeolite by weight of the membrane. It is well known in the field of alcohol fuel cells that PTFE does not conduct protons and cannot therefore be used as a membrane in the membrane electrode assembly of a fuel cell.

There have also been numerous methods involving including a zeolite material within the membrane itself of the PEM. For example, US2008/0070094 discloses an organic/inorganic composite electrolyte membrane formed by using zeolite as a hydrophilic organic particle in combination with a sulfonated fluorine-free polymer. The method comprises the steps of dissolving a sulfonated fluorine-free hydrocarbon based polymer into a solvent to provide a polymer solution, adding a zeolite thereto to form a dispersion, and then forming the inorganic/ organic composite electrolyte membrane from the composite solution. The problem addressed by this document is the provision of an electrolyte membrane which retains its proton conductivity even at low moisture content and high temperatures. The problem of alcohol crossover is not addressed in this document since the organic/inorganic composite electrolyte membrane formed is intended to be used in a hydrogen fuel cell rather than a direct methanol fuel cell (DMFC).

The present invention aims to overcome one or more of the above disadvantages of the prior art. It is therefore an aim to provide a proton exchange membrane having reduced alcohol (e.g. methanol) crossover as compared to conventional membranes. It is a further aim to provide a proton exchange membrane that is easy and economical to manufacture.

It is a further aim to provide a proton exchange membrane having a power density value comparable to or better than a conventional membrane.

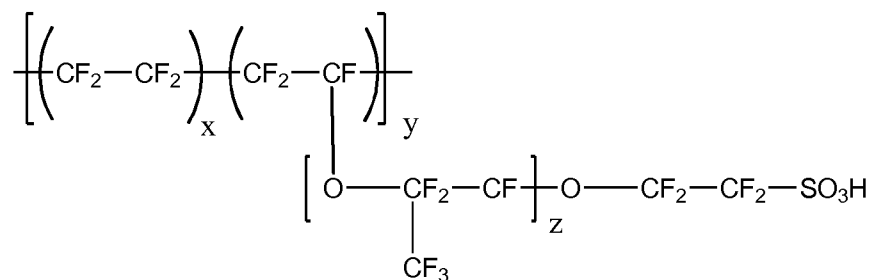
According to a first aspect of the present invention, there is provided a membrane electrode assembly comprising:

- 5 (a) a sulfonated fluoropolymer proton exchange membrane having one or more layers comprising a mixture of sulfonated fluoropolymer and a zeolite;
- (b) a cathode in contact with one face of the membrane;
- (c) an anode in contact with the other face of the membrane;

10 wherein the total zeolite content represents from 0.1 to 1.0% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers.

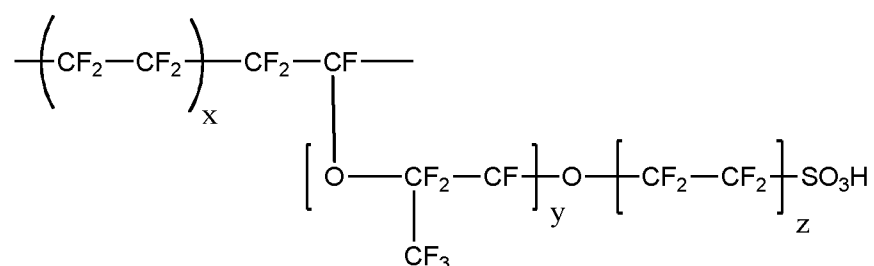
In an embodiment, the sulfonated fluoropolymer proton exchange membrane is a perfluorosulfonic acid membrane.

15 In an embodiment, the sulfonated fluoropolymer proton exchange membrane has a structure:



wherein $x = 5$, $y = 1000$ and $z = 3$ (for Nafion). Similar suitable membranes are described in Schultz et al; Chemical engineering and technology; 2001: 24(12): p1223-1233.

20 In an embodiment, the sulfonated fluoropolymer proton exchange membrane has a structure:



wherein; $x = 6$, $y = 1$ and $z = 1$ (for Nafion); or $x = 3-10$, $y=0.1$, $z=0-3$ (for Asahi Flemion); or $x = 2-14$, $y = 0.3$, $z = 1-2$ (for Aciplex-S). Similar suitable membranes are described in Micro fuel cells: principles and applications: T.S Zhao, 2009: p10.

In an embodiment, the perfluorosulfonic acid membrane is a commercially available membrane selected from the group consisting of: Nafion® (Du Pont), Dow membrane (Dow Chemical), Flemion membrane (Asahi Glass Co.), Aciplex membrane (Asahi Chem.), BAM (Ballarde), Solvay Hyflon and Gore-select membrane (W.L. Gore, Inc.). In a preferred embodiment, the sulfonated fluoropolymer proton exchange membrane is a Nafion® membrane. In a more preferred embodiment, the sulfonated fluoropolymer proton exchange membrane is Nafion® 117.

In an embodiment, the perfluorosulfonic acid membrane is a membrane selected from the group consisting of: sulphonated polyetheretherketone (sPEEK), sulphonated polysulphone (sPSU), sulphonated polyvinylacetate (sPVA), sulphonated polyetherimide (sPEI) and polybenzimidazole (PBI).

In an embodiment, the sulfonated fluoropolymer proton exchange membrane has a thickness of from 1 to 200µm. In an embodiment, the sulfonated fluoropolymer proton exchange membrane has a thickness of from 80 to 170µm. In an embodiment, the sulfonated fluoropolymer proton exchange membrane has a thickness of less than 80µm.

In an embodiment, each layer comprising a mixture of sulfonated fluoropolymer and a zeolite, provided as a mixture of the zeolite and monomer of the sulfonated fluoropolymer in one or more applications to the or each electrode, independently has a thickness of from 0.5µm to 15µm, preferably 1µm to 12µm.

The composition of the anode and cathode is entirely conventional. Thus, each electrode is formed from three component layers:

- (1) a thin porous layer, e.g. a carbon cloth or carbon paper, on which the remaining two layers are fabricated;
- (2) a gas diffusion layer composed of carbon particles along with a hydrophobic polymer (e.g. polytetrafluoroethylene (PTFE)); and
- (3) a catalyst layer.

In an embodiment, the structure, i.e. the composition layers (1) and (2), of the anode is identical to the structure, i.e. the composition layers (1) and (2), of the cathode.

In an embodiment, the catalyst material used in the catalyst layer of the anode is different from the catalyst material used in the catalyst layer of the cathode. In an embodiment, the catalyst material used in the catalyst layer of the cathode is platinum. In an embodiment, the catalyst material used in the catalyst layer of the anode is 1:1 Pt/Ru. In an embodiment, the catalyst material used in the catalyst layer of the anode is 2:1 Pt/Ru.

In an embodiment, the sulfonated fluoropolymer proton exchange membrane has one layer comprising a mixture of sulfonated fluoropolymer and a zeolite. In an embodiment, the face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the anode. In an embodiment, the face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the cathode. Preferably, the face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the anode. Results comparing the performance improvement of the layer comprising the mixture of sulfonated fluoropolymer and the zeolite being in contact with the anode and the cathode are illustrated in figures 24 and 25. It is thought that the improvement in performance for the anodic barrier placement (compared to the cathodic barrier placement) could be due to the retention of methanol at the anode which could improve performance due to increased uptake of the methanol at the anodic catalyst layer. This is particularly relevant at low molarities. The improvement could also be due to the prevention of methanol diffusion and prevention of saturation of methanol into the membrane.

In an alternative embodiment, the sulfonated fluoropolymer proton exchange membrane has two layers comprising a mixture of sulfonated fluoropolymer and a zeolite. In this embodiment, one face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the cathode and the other face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the anode. Figures 26 and 27 illustrate the improvement of the current and power densities for the MEAs having a barrier layer at both the anode and the cathode. It is thought that the improvement could be due to a reduction in methanol crossover. It is possible that a lower MOR loading could reduce the resistance of the MEA allowing for better proton transport. This is particularly relevant for the case in which the barrier layer is present at both the anode and the cathode. A reduction in MOR loading could improve DMFC performance when the crossover of methanol is not as prevalent due to the more efficient oxidation of the methanol at the catalyst layer.

In an embodiment, the sulfonated fluoropolymer of the mixture of sulfonated fluoropolymer and zeolite is the same sulfonated fluoropolymer as that of the proton exchange membrane. In an embodiment, the sulfonated fluoropolymer of the mixture of sulfonated fluoropolymer and zeolite is a perfluorosulfonic acid material such as Nafion® (Du Pont), Dow membrane (Dow Chemical), Flemion membrane (Asahi Glass Co.), Aciplex membrane (Asahi Chem.), BAM (Ballarde), Solvay Hyflon or Gore-select membrane (W.L. Gore, Inc.). In a preferred embodiment, the sulfonated fluoropolymer of the mixture of sulfonated fluoropolymer and zeolite is a Nafion® material. In a more preferred

embodiment, the sulfonated fluoropolymer of the mixture of sulfonated fluoropolymer and zeolite is Nafion® 117.

Zeolites are naturally occurring aluminosilicate crystals and have well defined and uniform pore size. As a result they can separate molecules based on their size and shape. They have high level of size selectivity in such separations and hence are called molecular sieves. The proportions of Si and Al atoms can be altered. This affects their hydrophobic/hydrophilic characters. These properties make them ideal candidates for use in the composite membranes of the present invention.

In an embodiment, the zeolite is selected from the group comprising: ZSM-5, zeolite A, zeolite X, zeolite Y, mordenite, AlPO_4 , SAPO, MeAlPO, SAPO-5, AIPO-5, VPI-5, MCM-41, chabazite, clinoptilolite, silica gel, zirconium-containing minerals, titanium-containing minerals, silicates and mixtures thereof. AlPO_4 , SAPO, MeAlPO, SAPO-5, AIPO-5, VPI-5, MCM-41 are all 'zeotype' materials (analogous of zeolites with different metals other than alumina-silicate, e.g. SAPO-5, AIPO-5 and VPI-5 are all analogous of zeolite ZSM-5 and have an MFI structure). In an embodiment, the titanium-containing mineral is an oxide of titanium i.e. a titanate. Preferably, the zeolite is mordenite. Natural mordenite has a Si/Al ratio of about 5. High purity synthesized mordenite has an increased Si/Al ratio of about 10 and high silica mordenites of having an Si/Al ratio of more than 40 are also known. Thus, in an embodiment, the mordenite has a Si/Al ratio of between about 5 and 40. In an embodiment, the mordenite has a Si/Al ratio of between about 5 and 20, preferably 10 and 15. In an embodiment, the mordenite has a Si/Al ratio of about 13. Other zeolites having a similar Si/Al ratio to that above would also be suitable for the membrane electrode assemblies of the present invention. In an embodiment, the zeolite is selected from the group comprising: zeolite-A ($\text{Si/Al} \geq 1$), zeolite-Y ($\text{Si/Al} \geq 2.5$), zeolite- β ($\text{Si/Al} \geq 8-20$), ZSM5 ($\text{Si/Al} \geq 10$), Chabazite ($\text{Si/Al} \geq 4$), Clinoptilolite ($\text{Si/Al} \geq 2$) and Faujasite ($\text{Si/Al} \geq 1.5$).

The ionic form and nature of the functionalisation of the zeolite can affect the performance of the MEA, for example, by improving methanol resistance of the MEA. This is demonstrated in example 11 for the zeolite, mordenite. In an embodiment, the zeolite is protonated zeolite. In an alternate embodiment, the zeolite is silane functionalised zeolite. In another alternate embodiment, the zeolite is sodium form zeolite.

The particle size of the zeolite employed in the barrier layer may be varied and may affect the performance of the MEA. In an embodiment, the particle size of the zeolite is < 500 nm, preferably < 400 nm, more preferably < 350 nm and yet more preferably < 300 nm. Figures 30 and 31 demonstrate that comparable DMFC performance can be achieved with both smaller and larger particles which demonstrates the broad range of zeolite particles sizes that can be employed in the MEAs of the present invention.

Figures 32 (a), (b) and (c) are SEM images of composite barrier layers featuring (a) FH-mordenite, (b) supernatant FH-mordenite with a particle size <300nm and (c) sprayed Nafion. (N.B. FH-mordenite stands for silane functionalised protonated mordenite.) Figure 32 (a) shows a dark band across the centre of the image. This indicates the presence of a layered structure when larger FH mordenite particles are employed. Figure 32 (b) shows a structure having greater homogeneity when using supernatant mordenite. It is possible that this could lead to further reductions in loading and therefore MEA resistance which in turn could give better DMFC performance. Figure 32 (c) is an SEM image of plain sprayed Nafion (i.e. having no particles present). The cracks in this image appear due to the intensity of the SEM beam.

As illustrated below in figures 15 - 17, the total zeolite content affects the power density of the resulting membrane electrode assembly. Surprisingly, it has been found that the narrow range of zeolite loading of the MEA of the present invention does not deleteriously affect the power density of the MEA. Further surprisingly, it has been found that the narrow range of zeolite loading of the MEA of the present invention actually improves the power density of the MEAs of the present invention when compared to conventional MEAs. This is entirely contrary to the prior art which teaches that the loading of zeolite in the MEAs actually lowers the power density.

Example 12 demonstrates the loading of the zeolite, mordenite, and its effects on the performance of the MEAs. For mordenite, the performance of the MEAs is improved for loading at 0.25, 0.5 and 0.75%. However, MEAs having a mordenite loading of 1% perform less favourably to MEAs having a loading of 0.25, 0.5 and 0.75%. The best performance improvement is achieved using a 0.5% mordenite loading.

In an embodiment, the total zeolite content represents between 0.1 and 1.0% (exclusive) by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers. In an embodiment, the total zeolite content represents from 0.25 to 0.75% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers. In a preferred embodiment, the total zeolite content represents from 0.4 to 0.6% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers. Preferably, the total zeolite content represents 0.5% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers.

According to a second aspect of the present invention, there is provided a process for preparing a membrane electrode assembly (MEA), the process comprising:

- (a) applying a mixture of a proton exchange membrane (PEM) polymer solution and a zeolite to a first electrode to form a layer of a composite on the first electrode, and optionally repeating the application of the mixture to the first electrode one or more times;
- 5 (b) providing a second electrode;
- (c) optionally applying a mixture of the proton exchange membrane (PEM) polymer solution and a zeolite to the second electrode to form a layer of a composite on the second electrode, and optionally repeating the application of the mixture to the second electrode one or more times;
- 10 (d) forming a membrane electrode assembly (MEA) by contacting a first face of a PEM with the first electrode and contacting a second face of the PEM with the second electrode.

In an embodiment, the application of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to the first electrode is repeated once, twice, three times, 15 four times, five times or six times. Thus two, three, four, five, six or seven layers of the mixture of the proton exchange membrane (PEM) monomer and the zeolite may be formed on the electrode. At certain concentrations of methanol, the optimum number of layers of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to a first electrode has been found to be four layers. This is illustrated in figure 28 (a1) and 20 (a2). At other concentrations of methanol, the optimum number of layers of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to a first electrode has been found to be more than four layers. For example, for 2M and 4M methanol concentration, the optimum number of layers has been found to be 5 layers. In an embodiment, therefore, the application of the mixture of the proton exchange membrane 25 (PEM) polymer solution and the zeolite to the first electrode is repeated three times.

Figure 28 shows that improvements were seen with all MEAs at temperatures above 40C.

Improvements seen with 0.375wt% mordenite (as a function of N117 weight) which was sprayed in three x 3ml aliquots are not as great as those with four or more layers (with solids composition of approximately 14% mordenite in Nafion).

30 Improvements seen with 0.5wt% mordenite (as a function of N117 weight) which was sprayed in seven aliquots are not as great as those using the traditional method (4x3ml aliquots to obtain a solids composition of approximately 14% mordenite in Nafion).

Improvements seen with 0.63wt% mordenite (as a function of N117 weight) which was sprayed in five x 3ml aliquots gives better performance than those using the traditional

method (4x3ml) at higher molarities of methanol. The solids composition of each layer is approximately 14% mordenite in Nafion.

In an embodiment, the first electrode is the anode and the second electrode is the cathode. In an alternative embodiment, the first electrode is the cathode and the second
5 electrode is the anode. Preferably, the first electrode is the anode and the second electrode is the cathode.

In an embodiment, the process does not include step (c). In this embodiment, only the first electrode includes the layer of a composite of the proton exchange membrane (PEM) polymer solution and the zeolite.

10 In an embodiment, the process does include step (c). In this embodiment, the process involves applying a mixture of the proton exchange membrane (PEM) monomer and a zeolite to the second electrode to form a layer of a composite on the second electrode. In an embodiment, the application of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to the second electrode is repeated once, twice, three
15 times, four times, five times or six times. Thus two, three, four, five, six or seven layers of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite may be formed on the second electrode. The optimum number of layers of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to the second electrode has been found to be four layers. In an embodiment, therefore, the application
20 of the mixture of the proton exchange membrane (PEM) polymer solution and the zeolite to the second electrode is repeated three times.

In an embodiment, the MEA is formed by hot pressing together the first electrode, PEM and second electrode so that the PEM is between the first electrode and the second electrode.

25 In an embodiment, the proton exchange membrane is a sulfonated fluoropolymer proton exchange membrane. Preferably, the sulfonated fluoropolymer proton exchange membrane is a perfluorosulfonic acid membrane.

Preferred membrane electrode assemblies that can be prepared using this process are described above in relation to the first aspect of the invention.

30 The process of the second aspect of the invention can be used to produce a membrane electrode assembly having a zeolite content in the range of 0.1 to 6.0% by weight of the sum of the proton exchange membrane and the solution polymer content of the one or more layers, preferably 0.1 to 3.0% and more preferably 0.25 to 2%. In an embodiment, the total zeolite content of the final MEA represents from 0.25 to 0.75% by weight of the
35 sum of the proton exchange membrane and the solution polymer content of the one or

more layers. In an embodiment, the total zeolite content represents from 0.4 to 0.6% by weight of the sum of the proton exchange membrane and the solution polymer content of the one or more layers. Preferably, the total zeolite content represents 0.5% by weight of the sum of the proton exchange membrane and the solution polymer content of the one or
5 more layers.

In an embodiment, the mixture of the PEM solution and zeolite is applied to the first electrode by spraying, immersion or spreading on with a blade. Preferably, the mixture of the PEM solution and zeolite is applied to the first electrode by spraying. Spraying provides a uniform layer of the mixture on the electrode.

10 In an embodiment, the mixture of the PEM solution and zeolite is applied to the second electrode by spraying, immersion or spreading on with a blade. Preferably, the mixture of the PEM solution and zeolite is applied to the second electrode by spraying.

The level of zeolite loading in the MEA is such that the layer allows protons through the membrane but impedes alcohol cross over through the membrane. Not meaning to be
15 bound by theory, it is considered that the hydrophilic particles each have a hydrophilic zone surrounding the particle. The desired level of hydrophilic particle loading provides an array of hydrophilic particles having overlapping hydrophilic regions to prevent alcohol crossover but large enough gaps between the particles to allow proton conduction to occur through the membrane.

20 When making the mixture to be applied to the PEM, the amount of zeolite in the PEM monomer / zeolite mixture is chosen such that the final MEA comprises from 0.1 to 6% by weight of the sum of the proton exchange membrane and the monomer of the one or more layers. This level of loading will depend on a number of factors including the thickness of the PEM including the proton conductivity/resistance, water uptake and methanol uptake of
25 the zeolite and the polymeric material used. Other preferred ranges of the amount of zeolite in the final MEA are described above.

The entire procedure for fabricating the MEA (including the steps of making the anode and cathode can be divided into three steps: (1) application of different layers onto the electrodes, (2) membrane treatment, and (3) integrating membrane and electrodes into
30 MEA. Individual steps involved in the preparation of MEA were:

1. Applying a gas diffusion layer (GDL);
2. Applying an anode catalyst layer;
3. Applying a cathode catalyst layer
4. Applying a bonding layer;

5. Applying a barrier layer (i.e. a layer of a composite including zeolite);
6. Membrane pre-treatment; and
7. MEA hot pressing.

Step 5 above was applied only to the composite MEA's and not to standard MEAs for comparison. When the barrier layer was used, the bonding layer was not applied separately. Application of each layer involved the same two steps. First was the preparation of ink containing the materials for the layer to be sprayed. These materials were dispersed in a solvent, which was used as a carrier for the materials.

It should also give appropriate viscosity to the ink necessary for spraying, must not react with the materials and should evaporate once sprayed onto the electrode. The second step in applying the layers was spraying the ink using the spray gun.

According to a third aspect of the present invention, there is provided a membrane electrode assembly obtainable by the process of the second aspect described above.

According to a fourth aspect of the present invention, there is provided a Direct Alcohol Fuel Cell (DAFC) comprising an MEA of the present invention.

In an embodiment, the DAFC is a DMFC. In an alternate embodiment, the DAFC is a direct ethanol fuel cell (DEFC).

MEA testing was carried out for standard MEA and the MEAs with barrier layer (Composite MEAs), in order to compare their DMFC performance. DMFC tests were carried out in a fuel cell testing unit, details of which are given below. The procedure followed for obtaining DMFC performance results is also given below.

The experimental setup can be divided into three categories for ease of explanation. First is the fuel cell testing unit where the MEAs were tested. Second is the electrical circuit which measured the voltage and current output of the MEA. Third is the reactant supply and product removal lines. Schematics of experimental setup are shown in figures 1 and 2. For the sake of clarity the electrical circuit is shown separately.

With reference to figure 1, liquid methanol and water was fed to the anode flowfield (AF) from methanol tank (MeOH Tank) using a peristaltic pump. Product stream from the anode was re-circulated back to the methanol tank. Change in methanol concentration for one run (one concentration of methanol run at different temperatures) was assumed to be insignificant to affect DMFC performance. Air from compressed cylinder was supplied to the cathode flowfield (CF). Its pressure and flow were measured by the flow meter and pressure gauge (see figure 1). Exit line from the cathode was sent to the drain. A heater was used to control the cell temperature. A temperature probe was used to measure the

anode flowfield temperature. This measurement was fed back to the heater which then controlled electrical supply to the heating plate in the cell. It was assumed that the temperature profile was the same in both flowfields and the temperature of the anode flowfield was the MEA temperature. This assumption can be justified by considering the high thermal conductivity of graphite flowfields

Figure 2 shows the electrical circuit. Anode flowfield of the cell (where oxidation takes place and hence electrons are generated) was connected to the positive terminal of the power supply. While the cathode flowfield (where reduction takes place and hence electrons are consumed) was connected to the negative of the power supply. A load was placed in the circuit to simulate a real load. An ammeter was connected in series with the power supply for measuring the current. While a voltmeter was connected in parallel to the cell to measure voltage.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention are further described hereinafter with reference to the accompanying drawings:

- Figure 1: Schematic of experimental setup showing testing unit and supply and removal lines.
- Figure 2: Schematic of experimental setup showing the electrical circuit.
- Figure 3: Plot of voltage against current density for standard MEA at 70°C and 1M methanol concentration in feed.
- Figure 4: Plot of voltage against current density for standard MEA at 1M methanol concentration in feed and at different temperatures.
- Figure 5: Plot of power density against current density for standard MEA at 1 M methanol concentration in feed at different temperatures.
- Figure 6: Plot of voltage against current density for standard MEA at 2 M methanol concentration in feed at different temperatures.
- Figure 7: Plot of power density against current density for standard MEA at 2 M methanol concentration in feed at different temperatures.
- Figure 8: Effect of concentration on cell voltage at 50°C.
- Figure 9: Effect of concentration on cell voltage at 70°C.
- Figure 10: Effect of concentration on cell voltage at 80°C.
- Figure 11: Effect of concentration on cell voltage at 90°C.

- Figure 12: Power density curves at different temperatures for MEA 0.25% and 2M methanol concentration in feed
- Figure 13: Comparison of power density curves for MEAs at 50°C and 1M methanol concentration in the feed
- 5 Figure 14: Comparison of power density curves for MEAs at 70°C and 1M methanol concentration in the feed
- Figure 15: Comparison of power density curves for MEAs at 90°C and 1M methanol concentration in the feed
- Figure 16: Comparison of power density curves for MEAs at 90°C and 2M methanol
10 concentration in the feed
- Figure 17: Comparison of power density curves for MEAs at 90°C and 4M methanol concentration in the feed
- Figure 18: Power density curves for MEA 0.5% at different temperatures and 5M methanol concentration in the feed
- 15 Figure 19: Power density curves for MEA 0.5% at different temperatures and 6M methanol feed.
- Figure 20: Comparison of power density curves for MEA 0% and MEA 0.5% at 60°C, 70°C and 80°C. Note that concentration of methanol feed to MEA 0% is 4M while that for MEA 0.5% is 5M.
- 20 Figure 21: An example procedure for silane functionalising of mordenite.
- Figure 22: An illustration of the chemical modification of zeolite surface by silane coupling agent GPTMS.
- Figure 23: XRD patterns of HMOR before and after silane functionalising.
- Figure 24: Illustrates that the power densities show improvements when the barrier
25 layer is placed at the anode or the cathode under all conditions when compared to the standard results from the application. The improvements are better when the layer is placed at the anode. Figure 24 (a) is for 1M, (b) is for 2M, (c) is for 4M methanol feeds for an MEA with 0.5% FMOR loadings at anode and cathode against standard Nafion 117.
- Figure 25: Illustrates that the current densities show improvement when the barrier
30 layer is placed at the anode for all conditions when compared to the standard results. The current density is improved when the barrier layer is placed at the cathode for 2M and 4M methanol flows, but not for 1M methanol flow. Figure 25 (a) is for 1M, (b) is for 2M, (c) is

for 4M methanol feeds for an MEA with 0.5% FMOR loadings at anode and cathode against standard Nafion 117.

Figure 26: Illustrates that the power densities show improvements when the barrier layer is placed at the anode and the cathode under all conditions when compared to the standard results. In this case, the MEAs having a barrier layer are loaded with 3mg of Pt and 0.5% MOR. Figure 26 (a) is for 1M, (b) is for 2M, (c) is for 4M, (d) is for 5M methanol feeds for MEA with 3mg platinum loadings against standard Nafion 117.

Figure 27: Illustrates that the current densities show improvements when the barrier layer is placed at the anode and the cathode under all conditions when compared to the standard results. In this case, the MEAs having a barrier layer are loaded with 3mg of Pt and 0.5% MOR. Figure 27 (a) is for 1M, (b) is for 2M, (c) is for 4M, (d) is for 5M methanol feeds for MEA with 3mg Pt loadings against standard Nafion 117.

Figure 28: Illustrates the improvement in (1) power density and (2) current density versus a standard MEA of novel MEAs using differing numbers of sprayed layers using (a) 1M, (b) 2M and (c) 4M methanol feeds.

Figure 29: Illustrates a comparison of the durability of a standard MEA and an MEA according to the present invention. The labels (A) to (D) on the figure represent:

- A) N117 beginning to fall below FMOR;
- B) Air supply exhausted, cells under hydration for 86h. Improvement under stop/start conditions better for FMOR;
- C) Air supply exhausted;
- D) High outlets from return to OCV and load cycle

Figure 30: Max power densities for (a) 1M, (b) 2M, (c) 4M methanol feeds for MEA with 0.5% normal (diamond) and supernatent (<300 nm) (square) mordenite loadings against standard Nafion 117.

Figure 31: Max current densities for (a) 1M, (b) 2M, (c) 4M methanol feeds for MEA with 0.5% normal (diamond) and supernatent (<300 nm) (square) mordenite loadings against standard Nafion 117.

Figure 32: SEM images of composite barrier layer featuring: (a) functionalised H-mordenite; (b) supernatent FH-mordenite with a particle size<300nm; (c) sprayed Nafion. (N.B. FH-mordenite stands for silane functionalised protonated mordenite.)

Figure 33: (a) 1M and (b) 2M DEFC performance using 0.5% silane functionalised mordenite as the barrier layer at various temperatures. (1) polarization curve and (2) power density curve.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of them mean "including but not limited to", and they are not intended to (and do not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

The invention will now be illustrated by way of the following non-limiting examples:

EXAMPLES

Example 1 – applying the gas diffusion layer (GDL)

Materials and quantity

- 5 Components of the GDL are ketjan black carbon and binding polymer, polytetrafluoroethylene (PTFE). The quantities required for GDL were calculated based on two main constraints,
- Carbon loading. It was desired to achieve a target of 1mg:cm^{-2} of carbon in the GDL.
 - 10 • Proportion of the binding polymer (PTFE). The binding polymer was desired to constitute 10% of GDL's weight, i.e.

$$\frac{PTFE}{Carbon + PTFE} = 10\%$$

- 15 A waste factor of 4 was used to allow for inevitable wastage of materials while spraying (maximum up to 4 times the target weight). Based on these constraints, following quantities of materials were used in preparing carbon ink,

- Note that the quantities mentioned above are for four electrodes (GDL at this stage) with a total area of 81cm^2 . The final electrodes were of dimensions $4.5\text{cm} \times$ applying the GDL it was cut into half prior to applying respective catalyst layers. This was done to simplify
- 20 fabrication procedures.

Carbon ink preparation

Carbon ink preparation Carbon ink for GDL was prepared according to the following steps,

1. The required amount PTFE was weighed in a bottle. PTFE was added to bind the carbon particles in GDL.
- 25 2. 5 mL of Isopropyl alcohol (IPA) was added and the mixture was sonicated for 10 minutes. This was done to disperse the PTFE before addition of carbon black. It is also easier and quicker to achieve uniformity at small volumes of solvent compared to large volumes. This homogeneity of PTFE is essential because it has to bind the carbon particles uniformly.
- 30 3. Required amount of carbon black was weighed.

4. After sonication of the IPA-PTFE mixture, this carbon black was added to it. Care was taken to add the carbon at the centre of the bottle. The resulting mixture was sonicated for 30 minutes.
5. After sonication large undissolved carbon particles were broken manually.
- 5 6. IPA was then added in small increments. During these IPA additions any carbon on the walls of the container were drawn back into the solution.

Table 3.1: Materials used for preparing carbon ink.

S No.	Material	Specification	Quantity
1	Carbon Black	None	324 mg
2	PTFE	60% wt solution	60 mg
3	IPA	None	60mL

- 10 7. The ink was sonicated for 30 minutes and the above steps 5 and 6 were repeated until all the remaining IPA was added. Note that the amount of IPA added after each sonication was incrementally raised from 2 mL to 5 mL by 1 mL at a time. Low volumes of solvent was added initially to achieve uniform dispersion of materials (same reasons as step 2).

15 **Spraying carbon ink**

Carbon and PTFE for GDL was applied by spraying according to the following steps,

1. The plain carbon paper (/backing layer) was first weighed. This is the foundation structure on which all layers of the electrodes are fabricated.
2. This was attached to the spraying platform which was heated to 60oC (to assist in evaporating the solvent, boiling point of IPA 82oC).
- 3 Airbrush was connected to the compressed nitrogen supply.
4. Carbon ink was sprayed in layers. Usually 3 mL of ink was sprayed per layer and it was dried in the oven at 110oC to completely remove residual solvent IPA). layer can be defined as the amount of materials deposited on the carbon paper before completely removing the solvent. This method was followed in order to achieve the target weight of materials for the whole GDL layer, by weighing each layer and calculating the required amount of ink to be sprayed after each layer.

5. Spraying was started by wetting the carbon paper with solvent. This would encourage the interaction between the first layer of the ink and the carbon paper. It was ensured that the backing layer was thoroughly wet by IPA.
6. Carbon ink was sprayed immediately following the previous step before the solvent evaporates. It was necessary to maintain right posture while spraying in order to ensure correct distance from the carbon paper and the angle of spraying. The distance between the nozzle of the airbrush and the carbon paper was approximately maintained around 2 cm and the airbrush was held at right angles to the carbon paper.
7. After spraying the first layer (3 mL), it was dried in the oven at 110°C for approximately 10 minutes (long enough to evaporate residual solvent).
8. The backing layer was weighed. From the weight increment, density of the ink was calculated and the amount required to achieve target weight was worked out.
9. Next layer was sprayed in the same way and the steps 6 to 9 were repeated until the target weight was achieved.
10. Once the target weight was achieved, the backing layer with GDL materials was sintered at 360°C for 1 hour in oven. Temperature was increased in a controlled manner from ambient temperature to 360°C for 1 hour and allowed to cool naturally in the oven.
11. Application for GDL was completed.

Example 2 – Applying catalyst layers

- Method of applying anode and cathode catalyst layers is similar. The materials required differ slightly but ink preparation and spraying are essentially the same. Materials and quantity for each electrode is given below. These are then followed by ink preparation and spraying.

Materials and quantity for anode

- Components of the anode are carbon supported Pt/Ru bi metal catalyst and Nafion, for binding the catalyst particles and to form the vital 3 phase region (between electrolyte, electrode and reactants, see figure 1.9). The quantities required for anode was calculated based on two main constraints,
- Platinum loading. It was desired to achieve a target of 1mg.cm^{-2} of platinum in the anode catalyst layer.
 - Proportion of Nafion. It was desired to constitute 15% of the weight of anode catalyst layer, i.e.

$$\frac{\text{Nafion}}{\text{Nafion} + \text{Pt} + \text{Ru} + \text{C}} = 15\%$$

As for carbon ink, as waste factor of 4 was used to allow for unavoidable wastage of materials while spraying (maximum up to 4 times the target weight). Based on these constraints, following quantities of materials were used in preparing anode catalyst ink,

Table 3.2: Materials used for preparing anode catalyst ink.

S No.	Material	Specification	Quantity
1	Pt-Ru/C catalyst	Pt:Ru – 40:20 and (Pt +Ru):C – 60:40	202.5 mg
2	Nafion	5% wt solution	714.7 mg
3	Acetone		60 mL

These quantities mentioned above were used for preparing anode ink for one electrode of dimensions 4.5cm x 4.5cm (i.e. area of 20.25cm²).

10 **Materials and quantity for cathode**

Components of cathode layer are carbon supported Pt catalyst and Nafion, for binding the catalyst particles and to form the vital 3 phase region. The quantities required for cathode was calculated based on two main constraints,

- Platinum loading. It was desired to achieve a target of 1mg.cm⁻² of platinum in the cathode catalyst layer.
- Proportion of Nafion. As for anode, it was desired to have Nafion as 15% of the weight of cathode catalyst layer, i.e.

$$\frac{\text{Nafion}}{\text{Nafion} + \text{Pt} + \text{C}} = 15\%$$

As for other inks, a waste factor of 4 was used to allow for wastage of materials while spraying. Based on these constraints, following quantities of materials were used in preparing cathode catalyst ink,

Table 3.3: Materials used for preparing cathode catalyst ink.

S No.	Material	Specification	Quantity
1	Pt/C catalyst	Pt:C – 60:40	135 mg
2	Nafion	5% wt solution	476.47 mg
3	Acetone		15 mL

The quantities mentioned above were used for preparing anode ink for one electrode of dimensions 4.5cm x 4.5cm (i.e. area of 20.25cm²).

5 Preparation of anode and cathode inks

Both catalyst inks were prepared according to the same given below,

1. The required quantity of Nafion was weighed in a vial.
2. To this, 14 mL of acetone was added.
3. The mixture was sonicated for 10 minutes. This was done to achieve
10 homogeneous distribution of Nafion in the ink (for the same reasons as for carbon ink mentioned in section 3.2.1).
4. The required quantity of catalyst (Pt-Ru/C for anode and Pt/C for cathode) was weighed separately.
5. After sonication of the initial acetone-Nafion mixture, the catalyst was gradually
15 added to it (to prevent it from dispersing else where, due to its fine nature).
6. This mixture was sonicated for 1 hour. Catalyst ink was then obtained.

Spraying catalyst Inks

Both catalyst inks were prepared Both catalyst inks were sprayed in a similar manner to carbon ink. The only differences were the use of acetone as solvent instead of IPA, the
20 platform was not heated (since acetone is more volatile than IPA), catalyst ink was sprayed on backing layer with GDL on it (not plain backing layer as for carbon ink) and eliminating the last sintering step at 360oC. When spraying was completed, the electrodes were dried in oven at 110oC, just like the drying step between each layer sprayed.

Example 3 – Applying bonding layer

25 Bonding layer was applied in between the electrode and the membrane. Its component is essentially Nafion.

Materials and quantity for bonding layer

Materials for bonding layer were calculated based on a target loading of $1\text{ mg}\cdot\text{cm}^{-2}$ of Nafion over the catalyst layer. The quantities are given below,

S No.	Material	Specification	Quantity
1	Pt/C catalyst	Pt:C – 60:40	135 mg
2	Nafion	5% wt solution	476.47 mg
3	Acetone		15 mL

- 5 A waste factor of 1.2 was included in the above calculations. These quantities are for one electrode of dimensions 4.5cm x 4.5cm.

Preparing bonding ink

Bonding ink was prepared according to the simple procedure given below,

- Required amount of Nafion was weighed into a vial.
- 10 • Desired amount of acetone was added and the mixture was sonicated for 15 minutes.

Spraying bonding layer

Bonding layer was sprayed according to the steps below,

1. The electrode was wet with acetone.
- 15 2. All of the bonding ink was sprayed as a single layer.
3. The electrode with the bonding layer was dried in an oven at between 100 and $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

Example 4 – application of barrier layer

- In this example, the barrier layer was applied only to the anodes of composite MEAs. This layer was essentially a modification of the bonding layer between the anode and membrane. The weight of mordenite required for this layer was too small to be measured accurately by the electronic weighing scale used. Hence a slurry containing acetone and ten times the weight of mordenite required in the ink was prepared. From this slurry the mordenite required for the barrier layers was transferred on a volumetric basis to a separate vial. To this vial the desired quantity of Nafion and acetone were added to make the mordenite ink to be sprayed as the barrier layer.

Components of the barrier layer were mordenite (functionalised and H^+ form) and Nafion. The weight of mordenite in the barrier layer to be sprayed on the electrode was calculated as a fraction of the weight of Nafion in the membrane, as follows,

$$\frac{\text{Mordenite}}{\text{Nafion in membrane} + \text{Mordenite}} = \text{desired weight\%}$$

- 5 The three composite MEAs had the following barrier layers, (where the % under Barrier layer column refers to the weight % of Nafion in Nafion 117 membrane),

Table 3.5: Barrier layers in composite MEAs

MEA	Barrier layer(s)
Composite MEA 1	one barrier layer of 0.25% mordenite.
Composite MEA 2	one barrier layer of 0.5% mordenite.
Composite MEA 3	one barrier layer of 0.25% mordenite and another of 0.5% mordenite.

Materials and quantity for barrier layer

- Three composite membranes containing the barrier layers (as given in table 3.5 above) were made from two mordenite inks of different composition. These inks were in turn made from the same slurry (different composition. These inks were in turn made from the same slurry (different volumes of slurry were taken for each ink). The composition of inks and slurries are given below,

Table 3.6: Composition of mordenite-acetone slurry

S No.	Material	Specification	Quantity Slurry
1	Mordenite	H^+ form and functionalised	36.9 mg
2	Acetone		10 mL

15

A waste factor of 4 was included in the mordenite inks in the above calculations. These quantities are for one electrode of dimensions 4.5cm x 4.5cm.

- The required amount of mordenite for the inks was transferred from the slurry on a volumetric basis, hence it was absolutely essential to ensure homogeneity of the slurry. For this reason the slurry was stirred using a magnetic stirrer for one hour, followed by sonication for 1 hour (in the sonicator) and magnetic stirring for one hour again. Basically macro mixing and micro mixing were done alternatively. This process was not done on the basis of optimising mixing of slurry hence the elaborate mixing time. After mixing the slurry

20

the required volume was immediately transferred into the vial for mordenite ink. The same mixing procedure was followed for mordenite ink to ensure homogeneity.

Table 3.7: Composition of mordenite ink 1 for 0.25% barrier layer

S No.	Material	Specification	Quantity mordenite ink 1
1	Mordenite-acetone slurry	refer table 3.6	2 mL
2	Nafion solution	5% wt	1.944 g
3	Acetone		approximately 20 mL

Table 3.8: Composition of mordenite ink 2 for 0.5% barrier layer

S No.	Material	Specification	Quantity mordenite ink 2
1	Mordenite-acetone slurry	refer table 3.6	4 mL
2	Nafion solution	5% wt	1.944 g
3	Acetone		approximately 20 mL

Spraying of Mordenite ink

- 5 The mordenite ink that was sprayed to obtain barrier layer, was continuously stirred before and during spraying. Mordenite ink was sprayed in multiple layers (similar to carbon and catalyst inks) according to the steps below,
 1. The electrode was wet with acetone.
 2. First layer of mordenite was sprayed. 3 mL of the ink was used for spraying initial layers.
 3. The electrode was dried in oven at 110°C for 10minutes to remove residual acetone.
 4. After drying, increase in weight of the electrode was calculated. The density of ink was obtained from this. From the target weight the amount of ink left to be sprayed was worked out. This calculation was done after every layer.
 5. Next layer was sprayed and the steps 2 and 3 above were repeated until the target weight for the barrier layer was reached.
 6. Barrier layer was obtained.

Example 5 – Membrane Pre-Treatment

- 20 Membrane pre-treatment was carried out in order to hydrate it, clean it and functionalise it. Details of materials used and procedure followed are given below,

Materials required

The only chemicals required for membrane pre-treatment were hydrogen peroxide and sulphuric acid. Solutions of required concentrations of these chemicals were prepared by diluting them in deionised water. The quantities of chemicals required to preparing 500 mL of the solutions are given in the table below,

Table 3.9: Materials required for membrane pre-treatment

S No.	Material	Specification	Concentration of solution	Quantity for 500 mL solution
1	Hydrogen peroxide	35% wt solution	5% volume	90.6 mL
2	Sulphuric acid	5% wt	1 M	26.65 mL

Deionised water was added to the above quantities to obtain solutions of desired volume.

Pre-treatment procedure

Standard Nafion membranes were treated as follows,

1. Nafion 117 membrane of the required size was cut.
2. This was then hydrated by boiling in deionised water for 10 minutes.
3. It was then heated in 5% volume H_2O_2 solution at 80°C for 30 minutes to remove any organic impurities.
4. It was then thoroughly washed in deionised water, twice at room temperature.
5. The membrane was then washed in deionised boiling water 3 times (10 minutes each time).
7. It was then stored in deionised water until its use.

Example 6 – Hot pressing

Three components (2 electrodes and membrane) were integrated to form the membrane electrode assembly (MEA) by hot pressing technique. In this method the three components are placed in order, heated and compressed for set time durations. A more elaborate procedure is given below,

1. The membrane electrode sandwich, was placed in between aluminium foil and stainless steel backing plates.
2. After arranging these layers as shown in the figure, they were held intact by PTFE tape. This was necessary to avoid displacement of any of the membrane-

electrode layers by shearing. If the alignment of any layer changes then effective electrode area would change and this will affect DMFC performance.

3. Pressure, temperature and time for the hot press were set as 3 bar, 135°C and 3 minutes respectively. Once the press was ready, the assembly was placed in it and pressed.
4. After execution of the above programme, settings were changed to cool the assembly to 66°C at 3 bar pressure and approximately within 30 minutes.
5. Once the assembly was cooled, the press was opened and the assembly was flipped, such that side of assembly in contact with the eater plate (upper one) ws faced down. This was done to ensure same level of hearing was given on both sides. Step 3 and 4 were then repeated.
6. After completion of the above programme, the assembly was taken out of the press and allowed to cool naturally to room temperature. The MEA can be taken out of the assembly.
7. The MEA is then placed in a fuel cell test unit and hydrated with deionised water.
8. After sufficient hydration (usually overnight) it is ready for use.

Example 7 – DMFC performance for MEAs

Performance test were carried out by varying one operating variable while holding others constant. Electrical output in terms of voltage and current were measured. Operating variables of significance were identified as methanol concentration in the feed and operating temperature of cell (Ge and Liu (2005)). All other variables including air flow rate, methanol flow rate, air and methanol pressure were held constant. These values are shown in the table below.

The concentration of oxygen in the air supply was assumed to be the same for

Table 3.10: Operating variables that were held constant through all DMFC performance runs

Operating variable	Value
Air flowrate	1 $L.min^{-1}$
Air pressure	2 bar
Methanol flowrate	5 $mL.min^{-1}$

all runs. One run was considered as the cell performance measured for a fixed methanol concentration and cell temperature. Methanol-water solution of desired concentration was

prepared and stored in the methanol tank from which it was pumped. Methanol and air were supplied to the cell at constant rates. The electrical circuit was broken initially to measure the open circuit voltage (OCV). The cell had some delay in attaining a stable OCV from start-up. This could have been due to unsteady state nature of methanol crossover through the cell. At the instant when the cell was started OCV was high. Then it steadily dropped to a stable value. This could be due to methanol crossover reaching steady state.

After OCV stabilised, the electrical circuit was re-established (i.e. connected). Current in the circuit was regulated by the power supply. From OCV state the current was increased by regular steps. When current was increase the voltage dropped. The current and voltage reading were noted. This step was repeated until voltage of the cell dropped to zero. Using the current and voltage data collected polarisation and power density curves were plotted.

Example 8 – Results for standard MEA

During DMFC testing, voltage (V) and current (A) produced by the MAE were noted. From this data current density (mA) and power density (mA) were calculated using the electrode area as follows,

$$\text{current density (mA.cm}^{-2}\text{)} = \frac{\text{current (mA)}}{\text{electrode area (cm}^2\text{)}} \quad (4.1)$$

$$\text{power (mW)} = \text{voltage (V)} \times \text{current (mA)} \quad (4.2)$$

$$\text{power density (mW.cm}^{-2}\text{)} = \frac{\text{power (mW)}}{\text{electrode area (cm}^2\text{)}} \quad (4.3)$$

$$(4.4)$$

Figure 3 shows the polarisation curve obtained for standard MEA at 70°C and 1M methanol concentration in the feed. The curve begins at an open circuit voltage (OCV) less than the theoretical value, then there is a step drop in voltage at low current densities followed by linear drop at mid current densities and terminated by faster drop in voltage (increasing gradient) at high current densities.

Effect of Temperature

Figure 4 below, shows the polarisation curves obtained at different temperatures and 1M methanol feed. Typical fuel cell behaviour is exhibited at all temperatures. In the figure below the curves at low temperatures appear to be linear through all the zones. This is because they are plotted together with those at higher temperatures which have large range for current density. If the low temperature curves are plotted individually then they closely represent typical fuel cell behaviour.

Figure 5 below is a plot of power density against current density for 1 M methanol feed at different temperatures. It can be seen that temperature affects two main values in the curve. They are maximum power density and limiting current density.

Figures 6 and 7 show the results obtained for 2 M methanol concentration in the feed. The same behaviour (as that for 1 M methanol feed) is evident.

Effect of Concentration

Figure 8 shows the effect of concentration on all voltage and power at 50°C.

Figure 9 shows the effect of concentration on cell voltage and power at 70°C. OCV decreases with increase in concentration of methanol. Also there is a decrease in voltage for the whole range. The decrease is much larger for 4 M than for 2 M. Same trends were observed for other temperatures. Thus methanol crossover affects performance at all currents and temperatures. Power density changes according to change in voltage at the same current. Hence polarisation curves for other temperatures are plotted without the power density. This also shows other features in the polarisation curves more clearly. The decrease in OCV and voltage at lower current densities, with increase in methanol concentration, indicate that MCO detrimentally affects performance.

Figure 10 shows the effect of concentration on all voltage and power at 80°C.

Figure 11 shows the effect of concentration on all voltage and power at 90°C.

Example 9 - Result for composite MEAs

For convenience the following abbreviations for the different membrane electrode assemblies will be used in the following discussion (and in subsequent sections as well):

- Membrane electrode assembly with standard Nafion 117 but no barrier layer – MEA 0%
- Membrane electrode assembly with Nafion 117 and barrier layer containing 0.25% wt mordenite with respect to the weight of Nafion in the Nafion 117 membrane – MEA 0.25%
- Membrane electrode assembly with Nafion 117 and a barrier layer containing 0.5% wt mordenite with respect to the weight of Nafion in the Nafion 117 membrane – MEA 0.5%

The effects of temperature and concentration on performance were similar for both composite MEAs. However with temperature, performance improved up to a certain temperature and declined at higher temperatures. An example of this behaviour can be

seen from figure 12, the power density curve for MEA 0.25% for 2M concentration of methanol in the feed.

Example 10 - Comparison of results for composite and standard membrane electrode assemblies.

- 5 Power density curves are used to present the results for different MEAs. Composite MEAs showed significant improvement in performance (especially MEA 0.5%) at all temperatures and methanol concentrations compared to the standard MEA with no barrier layer. MEA 0.5% had better performance than MEA 0.25%, indicating that performance improves with mordenite concentration in the barrier layer. Figures 13, 14 and 15 compare the power
10 density curves at 50°C, 70°C and 90°C for 1M methanol concentration in the feed. These figures are an example of improvement in performance across all temperatures.

- Biggest improvements were attained at 90°C. Figures 16 and 17 below show the improvement at 90°C for 2M and 4M methanol concentration in the feed. The OCV and maximum power density for all temperatures, methanol concentrations and MEAs are
15 given in tables 4.1, 4.2 and 4.3 below.

The composite MEA 0.5% was also run at 5M and 6M methanol concentration in the feed. The standard MEA 0% performed very poorly at 4M methanol concentration in the feed due to high methanol crossover. The power density results for MEA 0.5% at 5M and 6M methanol concentration in the feed is given in figures 19 and 20 below.

- 20 These results show a superior performance of composite MEA 0.5% over standard MEA 0%. This is clear by comparing power density curves for standard MEA 0% at 4M with that of MEA 0.5% at 5M. This comparison is shown in figure 20. The maximum power density values are summarised and compared in table 4.4 below.

	OCV (V)	% Change in OCV	P_{max} (mW/cm ²)	% Change in P_{max}	% Change in P_{max} (w.r.t MEA 0%)
T = 30C					
MEA 0%	0.544		7.88		
MEA 0.25%	0.543	0%	8.26	5%	5%
MEA 0.5%	0.563	4%	10.86	32%	38%
T = 40C					
MEA 0%	0.557		10.70		
MEA 0.25%	0.568	2%	14.77	38%	38%
MEA 0.5%	0.575	1%	16.97	15%	59%
T = 50C					
MEA 0%	0.572		15.20		
MEA 0.25%	0.565	-1%	18.09	24%	24%
MEA 0.5%	0.581	3%	23.31	23%	53%
T = 60C					
MEA 0%	0.579		19.61		
MEA 0.25%	0.571	-1%	24.79	26%	26%
MEA 0.5%	0.594	4%	31.46	27%	60%
T = 70C					
MEA 0%	0.565		24.53		
MEA 0.25%	0.582	3%	31.66	29%	29%
MEA 0.5%	0.607	4%	39.41	24%	61%
T = 80C					
MEA 0%	0.601		31.95		
MEA 0.25%	0.592	-1%	36.59	15%	15%
MEA 0.5%	0.618	4%	46.61	27%	46%
T = 90C					
MEA 0%	0.603		32.22		
MEA 0.25%	0.587	-3%	36.75	14%	14%
MEA 0.5%	0.618	5%	50.77	38%	58%

Table 4.1: Summary and comparison of open circuit voltage (V), OCV and maximum power density (mW=cm²), P_{max} , for all MEAs at 1 M methanol feed concentration and different temperatures

MEA and Temperature	OCV (V)	% Change in OCV	P_{max} (mW/cm ²)	% Change in P_{max}	% Change in P_{max} (w.r.t MEA 0%)
T = 30C					
MEA 0%	0.464		8.41		
MEA 0.25%	0.531	14%	9.45	12%	12%
MEA 0.5%	0.515	3%	10.37	10%	23%
T = 40C					
MEA 0%	0.481		12.10		
MEA 0.25%	0.515	7%	14.07	16%	16%
MEA 0.5%	0.500	4%	16.20	15%	34%
T = 50C					
MEA 0%	0.516		17.80		
MEA 0.25%	0.527	2%	18.40	3%	3%
MEA 0.5%	0.555	5%	24.34	32%	37%
T = 60C					
MEA 0%	0.532		22.50		
MEA 0.25%	0.545	2%	24.08	7%	7%
MEA 0.5%	0.566	4%	31.94	33%	42%
T = 70C					
MEA 0%	0.538		25.60		
MEA 0.25%	0.55	2%	27.47	7%	7%
MEA 0.5%	0.576	5%	39.03	42%	52%
T = 80C					
MEA 0%	0.529		23.94		
MEA 0.25%	0.556	5%	26.71	12%	12%
MEA 0.5%	0.570	4%	44.27	66%	85%
T = 90C					
MEA 0%	0.509		16.30		
MEA 0.25%	0.526	3%	22.67	39%	39%
MEA 0.5%	0.567	8%	39.96	76%	145%
Maximum values	0.576	14%	44.27	76%	145%

Table 4.2: Summary and comparison of open circuit voltage (V), OCV and maximum power density (mW=cm²), P_{max} , for all MEAs at 2 M methanol feed concentration and

5 different temperatures

MEA and Temperature	OCV (V)	% Change in OCV	P_{max} (mW/cm ²)	% Change in P_{max}	% Change in P_{max} (w.r.t MEA 0%)
T = 30C					
MEA 0%	0.46		6.22		
MEA 0.25%	0.466	1%	7.70	25%	25%
MEA 0.5%	0.506	9%	10.02	29%	61%
T = 40C					
MEA 0%	0.46		9.24		
MEA 0.25%	0.465	1%	11.30	23%	23%
MEA 0.5%	0.533	15%	15.11	33%	63%
T = 50C					
MEA 0%	0.49		12.51		
MEA 0.25%	0.486	1%	14.52	16%	16%
MEA 0.5%	0.55	13%	20.40	41%	64%
T = 60C					
MEA 0%	0.5		14.54		
MEA 0.25%	0.504	1%	18.39	26%	26%
MEA 0.5%	0.552	10%	25.20	37%	70%
T = 70C					
MEA 0%	0.484		10.18		
MEA 0.25%	0.491	1%	18.49	76%	76%
MEA 0.5%	0.563	15%	30.42	65%	190%
T = 80C					
MEA 0%	0.472		7.96		
MEA 0.25%	0.454	-4%	14.70	85%	85%
MEA 0.5%	0.524	15%	24.77	68%	211%
T = 90C					
MEA 0%	0.392		3.29		
MEA 0.25%	0.39	-1%	9.04	175%	175%
MEA 0.5%	0.432	11%	14.67	62%	346%
Maximum values	0.563	15%	30.42	175%	346%

Table 4.3: Summary and comparison of open circuit voltage (V), OCV and maximum power density (mW=cm²), P_{max} , for all MEAs at 4 M methanol feed concentration and different temperatures

MEA / Temperature ($^{\circ}\text{C}$)	P_{max} (mW/cm 2)	% Increase in P_{max}
T = 60$^{\circ}\text{C}$		
MEA 0% (4M)	14.54	
MEA 0.5% (5M)	22.02	51%
T = 70$^{\circ}\text{C}$		
MEA 0% (4M)	10.48	
MEA 0.5% (5M)	23.36	123%
T = 80$^{\circ}\text{C}$		
MEA 0% (4M)	7.96	
MEA 0.5% (5M)	16.70	110%

Table 4.4: Comparison of maximum power density (mW=cm 2), P_{max} achieved for MEA 0% at 4 M methanol feed and MEA 0.5% 5M methanol feed. The third column shows the increase in P_{max} for MEA 0.5% as a percentage of P_{max} value for MEA 0%.

Summary

From these results it can be concluded that the barrier layer in composite MEAs is effective in reducing methanol crossover without adversely affecting proton conductivity. This is strongly proved by the superior performance of MEA 0.5% at 5M compared to the reasonable performance of standard MEA to a maximum concentration of 4M. Hence the research objective of reducing methanol crossover without affecting proton conductivity seems to have been achieved. The performance of standard MEA was repeated by fabricating a new MEA and the results obtained at selected temperatures and concentrations, agreed closely with those obtained by the first standard MEA. This confirms the performance of standard MEA and hence the improvement in performance with barrier layers. The combined effect of change in methanol crossover the proton conductivity by the inclusion of barrier layer is positive. This is directly proved by the superior performance of composite MEAs.

Example 11: effect on the performance of an MEA due to the ionic form and nature of the silane functionalisation of mordenite

This example demonstrates the effect on the performance of an MEA due to the mordenite ionic form and nature of the silane functionalisation of the mordenite. In these examples, mordenite is ground before using and undergoes an ion-exchange reaction (by treatment with conc. H_2SO_4). As can be seen from the results below, better performance is obtained with all of the MEAs according to the present invention, especially at higher temperatures. The improvement in performance at higher temperatures is thought to be due to more

facile anode kinetics and increased amounts of methanol crossover. The MEAs according to the present invention are able to reduce the increased methanol crossover at the higher temperatures relative to the methanol fuel crossover of conventional MEAs.

The below tables show peak power densities and peak current densities for each MEA.

5 The following abbreviations are used:

FH=silane functionalised protonated mordenite: particle size≈300nm

H=Protonated mordenite

Na=Sodium form mordenite

(G) = particle size≈300nm

10 (C) = particle size≈3000nm

1M METHANOL FEED

MEA REF	TEMP C	OCV mV	PEAK POWER DENSITY mW cm ²	PEAK CURRENT DENSITY mA cm ²	POWER DENSITY AT N117 CURRENT DENSITY mW cm ²
N117	40	553	16.119	79.012	16.119
	50	572	21.768	93.827	21.768
	60	580	26.942	115.556	26.942
	70	597	30.495	130.864	30.495
	80	608	33.511	128.395	33.511
	90	611	34.8	143.21	34.8
0.5%FH(G)	40	559	19.081	69.136	17.826
	50	583	26.222	88.889	26.178
	60	595	34.086	123.951	33.8
	70	606	43.556	148.148	40.7
	80	613	51.911	177.778	46.094
	90	636	50.765	197.53	57.546
0.5%H(G)	40	575	20.227	79.012	20.227
	50	596	25.857	83.951	25.709
	60	602	32.77	103.704	32.2
	70	608	38.519	118.519	36.4
	80	604	41.63	148.148	40.573
	90	606	45.375	193.086	41.674
0.5%H(C)	40	583	18.849	64.198	16.435
	50	595	25.101	83.951	24.489
	60	598	31.506	108.642	30.4
	70	599	35.679	123.457	35.1

	80	604	39.548	138.765	39.3
	90	599	41.472	167.901	40.5
0.5%Na(G)	40	563	14.341	59.259	9.877
	50	572	19.686	74.568	16.42
	60	589	25.778	98.765	22
	70	598	31.916	113.58	30.5
	80	597	36.464	128.395	34.464
	90	603	43.674	162.963	42.9
0.5%Na(C)	40	542	19.674	59.259	2.607
	50	573	26.667	74.074	14.82
	60	590	33.956	94.321	28.1
	70	601	39.185	113.58	38.5
	80	601	47.111	148.148	45.709
	90	599	48.563	162.963	46.543

2M METHANOL FEED

MEA REF	TEMP C	OCV mV	PEAK POWER DENSITY mW cm ²	PEAK CURRENT DENSITY mA cm ²	POWER DENSITY AT N117 CURRENT DENSITY mW cm ²
N117	40	526	19.342	100.741	19.342
	50	545	24.382	104.398	24.382
	60	572	27.188	122.469	27.188
	70	583	30.044	128.395	30.044
	80	573	27.751	124.444	27.751
	90	436	17.462	83.951	17.462
0.5%FH(G)	40	531	23.028	109.136	22.1
	50	565	32.332	138.765	28.7
	60	582	40.632	167.901	33.7
	70	591	44.72	173.333	40.8
	80	593	44.267	177.778	39.1
	90	551	20.299	109.136	18.553
0.5%H(G)	40	569	24.578	103.574	24.4
	50	580	30.42	138.272	28.9
	60	592	36.662	143.21	35.2
	70	589	38.622	162.963	36.849
	80	596	37.778	148.148	36.1
	90	539	26.923	143.21	25.5
0.5%H(C)	40	536	21.136	98.765	21.2
	50	587	32.533	133.33	29.8
	60	592	35.298	178.272	32.5
	70	596	39.763	162.963	37.748

	80	559	41.309	172.84	37.4
	90	513	31.545	158.519	25.6
0.5%Na(G)	40	525	18.889	83.951	16.6
	50	545	26.083	109.136	25.9
	60	555	34.983	138.272	33.4
	70	576	39.318	162.469	37.363
	80	568	42.973	187.654	38.8
	90	508	19.733	88.889	19.644
0.5%Na(C)	40	513	16.356	79.012	14.7
	50	533	20.6	93.827	19.6
	60	546	26.785	118.519	26.7
	70	563	30.765	172.84	28.632
	80	553	26.932	143.21	26.1
	90	513	19.753	98.765	19.225

4M METHANOL FEED

MEA REF	TEMP	OCV	PEAK POWER DENSITY	PEAK CURRENT DENSITY	POWER DENSITY AT N117 CURRENT DENSITY
	C	mV	mW cm ²	mA cm ²	mW cm ²
N117	40	482	13.63	74.074	13.63
	50	509	17.881	83.951	17.881
	60	525	20.475	99.259	20.475
	70	523	22.402	104.198	22.402
	80	470	8.356	59.259	8.356
	90	336	6.716	49.384	6.716
0.5%FH(G)	40	475	18.109	93.827	15.63
	50	515	24.193	113.58	20.401
	60	526	26.087	114.074	25.1
	70	557	28.765	123.457	28.1
	80	423	13.906	108.642	12.148
	90	339	6.775	69.136	6.222
0.5%H(G)	40	519	17.077	93.827	16.37
	50	571	25.896	113.58	24.178
	60	573	27.714	113.58	27
	70	564	25.737	104.198	25.737
	80	504	19.081	118.518	15.052
	90	357	7.037	74.074	6.519
0.5%H(C)	40	526	19.455	99.259	18.444
	50	530	23.748	103.704	22.667
	60	537	27.517	123.951	27.098
	70	543	31.936	143.21	30.009

	80	460	16.8	103.704	13.807
	90	374	7.062	64.198	6.568
0.5%Na(G)	40	513	17.077	93.827	16.37
	50	528	22.373	109.136	21.6
	60	541	25.6	118.519	24.3
	70	554	24.962	114.074	24.5
	80	494	21.63	98.765	17.481
	90	368	7.506	64.198	6.42
0.5%Na(C)	40	519	14.38	69.136	14
	50	538	19.309	83.951	19.309
	60	541	21.926	98.765	21.9
	70	517	20.079	93.827	19.902
	80	420	9.694	64.198	9.422
	90	368	6.138	54.321	6.074

As can be seen above, improved performance was obtained when using 0.5% mordenite which has undergone treatment with a silane functionalising agent. It is thought that the silane functionalisation promotes interfacial adhesion between the inorganic and the organic media thereby improving the methanol resistance of the MEA. Like for like
 5 improvements of 59.5% in power density achieved at 80C with a 2M methanol feed.

Example 12: the effect of silane functionalised mordenite loading.

This example demonstrates the effect the level of loading of the silane functionalised mordenite has on the performance of the MEAs. As can be seen from the results below,
 10 the performance of the MEAs is improved for loading of silane functionalised mordenite at 0.25, 0.5 and 0.75%. However, MEAs having a silane functionalised mordenite loading of 1% perform less favourably to MEAs having a loading of 0.25, 0.5 and 0.75%.

It can also be seen that the improved performance is particularly exhibited at higher temperatures. The improvement in performance at higher temperatures is thought to be
 15 due to more facile anode kinetics and increased amounts of methanol crossover. The MEAs according to the present invention are able to reduce the increased methanol crossover at the higher temperatures relative to the methanol fuel crossover of conventional MEAs.

The best performance improvement is achieved using a 0.5% mordenite loading. This is
 20 thought to be due to the favourable dispersion of mordenite within the layers. The following abbreviations are used:

FH=silane functionalised protonated mordenite: particle size≈300nm

1M METHANOL FEED

MEA REF	TEMP	OCV	PEAK POWER DENSITY	PEAK CURRENT DENSITY	POWER DENSITY AT N117 CURRENT DENSITY
	C	mV	mW cm ²	mA cm ²	mW cm ²
N117	40	538	16.119	79.012	16.119
	50	562	21.768	93.827	21.768
	60	583	26.942	115.556	26.942
	70	590	30.495	130.864	30.495
	80	580	33.511	128.395	33.511
	90	570	34.8	143.21	34.8
0.25%FH	40	567	14.765	64.198	13.195
	50	568	18.889	74.074	17.45
	60	573	25.511	103.704	24.4
	70	589	31.664	138.272	31.54
	80	598	36.588	153.086	35.565
	90	591	37.087	153.086	36.52
0.5%FH	40	575	19.081	69.136	17.826
	50	580	26.222	88.889	26.178
	60	595	34.086	123.951	33.8
	70	606	43.556	148.148	40.7
	80	613	51.911	177.778	46.094
	90	636	50.765	50.765	57.546
0.75%FH	40	594	14.188	69.136	13.274
	50	599	24.02	79.012	23.457
	60	608	29.97	103.704	28.3
	70	615	36.267	133.827	36.2
	80	615	41.917	146.667	41
	90	616	43.658	169.877	42.82
1%FH	40	614	13.156	44.444	3.398
	50	624	15.072	69.136	6.9
	60	630	17.965	83.951	9
	70	630	19.63	74.074	7.1
	80	635	19.811	79.012	9.7
	90	624	20.232	83.951	2

2M METHANOL FEED

MEA REF	TEMP	OCV	PEAK POWER DENSITY	PEAK CURRENT DENSITY	POWER DENSITY AT N117 CURRENT DENSITY
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	C	mV	mW cm ²	mA cm ²	mW cm ²
N117	40	526	19.342	100.741	19.342
	50	545	24.382	104.398	24.382
	60	572	27.188	122.469	27.188
	70	583	30.044	128.395	30.044
	80	573	27.751	124.444	27.751
	90	436	17.462	83.951	17.462
0.25%FH	40	515	16.625	89.383	16
	50	524	22.504	103.704	22.5
	60	546	27.284	123.457	27.2
	70	550	31.585	128.395	31.585
	80	554	30.533	133.333	30.4
	90	533	18.4	88.899	18.133
0.5%FH	40	531	23.028	109.136	22.1
	50	565	32.332	138.765	28.7
	60	582	40.632	167.901	33.7
	70	591	44.72	173.333	40.8
	80	593	44.267	177.778	39.1
	90	551	20.299	109.136	18.553
0.75%FH	40	575	22.209	98.272	22.1
	50	582	29.156	118.519	28.2
	60	588	33.973	124.444	33.8
	70	597	39.467	146.473	38.5
	80	591	43.631	173.827	39.6
	90	527	34.077	157.037	26.696
1%FH	40	512	19.98	83.951	19.7
	50	536	24.778	110.617	24.4
	60	565	26.897	119.012	26.3
	70	594	26.331	118.519	26.06
	80	592	21.57	103.704	20
	90	557	11.437	59.259	9.822

4M METHANOL FEED

MEA REF	TEMP	OCV	PEAK POWER DENSITY	PEAK CURRENT DENSITY	POWER DENSITY AT N117 CURRENT DENSITY
	C	mV	mW cm ²	mA cm ²	mW cm ²
N117	40	482	13.63	74.074	13.63
	50	509	17.881	83.951	17.881
	60	525	20.475	99.259	20.475
	70	523	22.402	104.198	22.402
	80	470	8.356	59.259	8.356

	90	336	6.716	49.384	6.716
0.25%FH	40	458	14.523	83.951	16
	50	481	19.358	98.765	22.5
	60	494	24.193	113.58	27.2
	70	526	26.543	123.457	31.585
	80	499	13.906	108.642	30.4
	90	335	6.499	69.136	18.133
0.5%FH	40	475	18.109	93.827	22.1
	50	515	24.193	113.58	28.7
	60	526	26.087	114.074	33.7
	70	557	28.765	123.457	40.8
	80	423	14.775	108.642	39.1
	90	339	6.775	69.136	18.553
0.75%FH	40	533	14.188	64.198	22.1
	50	551	17.407	74.074	28.2
	60	553	20.316	83.951	33.8
	70	557	21.926	98.765	38.5
	80	423	12.167	94.321	39.6
	90	329	6.573	54.321	26.696
1%FH	40	540	14.815	74.074	19.7
	50	555	16.978	88.998	24.4
	60	568	19.336	94.321	26.3
	70	557	19.891	93.827	26.06
	80	475	7.887	59.753	20
	90	333	6.193	54.321	9.822

Example 13 – Effect of mordenite particle size on DMFC performance

This example demonstrates that comparable improvement in MEA performance can be achieved when MEAs utilising different sizes of mordenite are employed. During the manufacture of the MEA, a mordenite slurry of 1% wt/vol was sonicated for 10 minutes. The sonicated slurry was allowed to settle and the larger particles were allowed to drop to bottom of vessel. The solid content was measured. A 0.5wt% ink was sprayed onto the anode using the procedure given above in example 4. As can be seen from figures 30 and 31 comparable current and power density plots were obtained.

Example 14 – results for composite MEAs in a direct ethanol fuel cell

An MEA of the present invention having 0.5% silane functionalised mordenite as the barrier layer was tested in a direct ethanol fuel cell (DEFC) and the results are given in figure 33. Although the results obtained for a direct ethanol fuel cell (DEFC) have around

1/5 the power density of a DMFC, this example demonstrates that the MEAs of the present invention may be used in a DEFC.

CLAIMS:

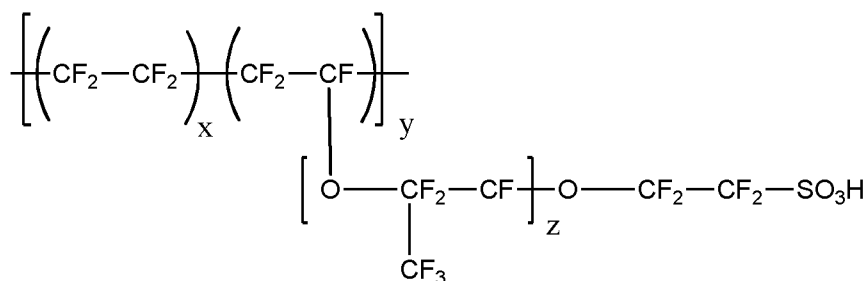
1. A membrane electrode assembly comprising:

- 5 a) a sulfonated fluoropolymer proton exchange membrane having one or more layers comprising a mixture of sulfonated fluoropolymer and a zeolite;
- b) a cathode in contact with one face of the membrane;
- c) an anode in contact with the other face of the membrane;

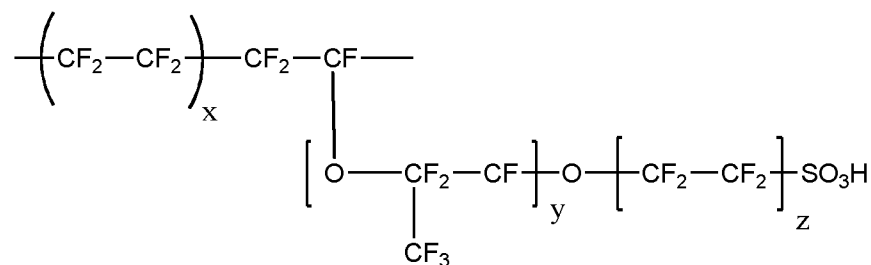
10 wherein the total zeolite content represents from 0.1 to 1.0% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers.

2. The membrane electrode assembly of claim 1 wherein the face of the membrane having a layer comprising a mixture of sulfonated fluoropolymer and a zeolite is in contact with the anode.

15 3. The membrane electrode assembly of claim 1 or claim 2 wherein the sulfonated fluoropolymer proton exchange membrane is a perfluorosulfonic acid membrane, optionally wherein the sulfonated fluoropolymer proton exchange membrane has a structure:



wherein $x = 5$, $y = 1000$ and $z = 3$, or



20

wherein; $x = 6$, $y = 1$ and $z = 1$; or $x = 3-10$, $y=0.1$, $z=0-3$; or $x = 2-14$, $y = 0.3$, $z = 1-2$.

4. The membrane electrode assembly of claim 3 wherein the perfluorosulfonic acid membrane is selected from the group consisting of: Nafion® (Du Pont), Dow membrane

(Dow Chemical), Flemion membrane (Asahi Glass Co.), Aciplex membrane (Asahi Chem.), BAM (Ballarde), Solvay Hyflon and Gore-select membrane (W.L. Gore, Inc.).

5. The membrane electrode assembly of any preceding claim wherein the sulfonated fluoropolymer of the mixture of sulfonated fluoropolymer and zeolite is the same sulfonated fluoropolymer as that of the proton exchange membrane.

6. The membrane electrode assembly of any preceding claim wherein the zeolite is selected from the group consisting of: mordenite, zeolite-A ($\text{Si}/\text{Al} \geq 1$), zeolite-Y ($\text{Si}/\text{Al} \geq 2.5$), zeolite- β ($\text{Si}/\text{Al} \geq 8-20$), ZSM5 ($\text{Si}/\text{Al} \geq 10$), Chabazite ($\text{Si}/\text{Al} \geq 4$), Clinoptilolite ($\text{Si}/\text{Al} \geq 2$) and Faujasite ($\text{Si}/\text{Al} \geq 1.5$).

7. The membrane electrode assembly of any preceding claim wherein the total zeolite content represents from 0.25 to 0.75% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers.

8. The membrane electrode assembly of claim 7 wherein the total zeolite content represents 0.5% by weight of the sum of the sulfonated fluoropolymer proton exchange membrane and the sulfonated fluoropolymer of the one or more layers.

9. A process for preparing a membrane electrode assembly (MEA), the process comprising:

(a) applying a mixture of a proton exchange membrane (PEM) monomer and a zeolite to a first electrode to form a layer of a composite on the first electrode, and optionally repeating the application of the mixture to the first electrode one or more times;

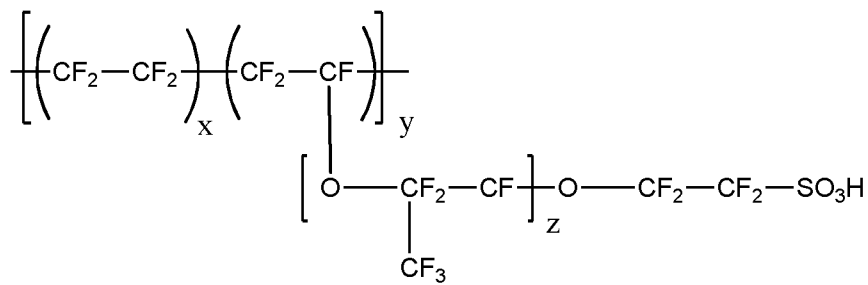
(b) providing a second electrode;

(c) optionally applying a mixture of the proton exchange membrane (PEM) monomer and a zeolite to the second electrode to form a layer of a composite on the second electrode, and optionally repeating the application of the mixture to the second electrode one or more times;

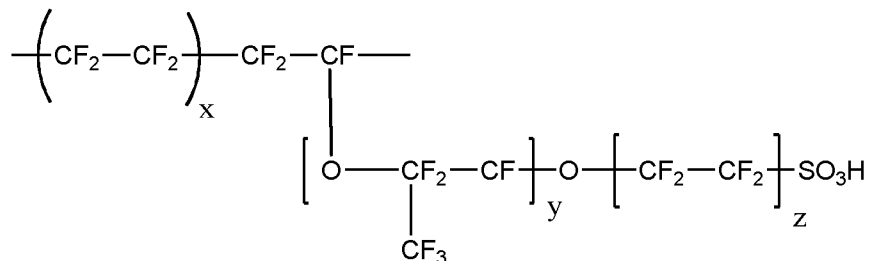
(d) forming a membrane electrode assembly (MEA) by contacting a first face of a PEM with the first electrode and contacting a second face of the PEM with the second electrode.

10. The process of claim 9 wherein the application of the mixture of the proton exchange membrane (PEM) monomer and the zeolite to the first electrode is repeated once, twice, three times, four times, five times or six times, preferably three times.

11. The process of claim 9 or claim 10 wherein the first electrode is the anode and the second electrode is the cathode.
12. The process of any of claims 9 to 11 wherein the process does not include step (c).
13. The process of any of claims 9 to 12 wherein the MEA is formed by hot pressing together the first electrode, PEM and second electrode so that the PEM is between the first electrode and the second electrode.
14. The process of any of claims 9 to 13 wherein the proton exchange membrane is a sulfonated fluoropolymer proton exchange membrane, optionally a perfluorosulfonic acid membrane.
- 10 15. The process of any of claim 14 wherein the sulfonated fluoropolymer proton exchange membrane has a structure:



wherein $x = 5$, $y = 1000$ and $z = 3$, or



- 15 wherein; $x = 6$, $y = 1$ and $z = 1$; or $x = 3-10$, $y=0.1$, $z=0-3$; or $x = 2-14$, $y = 0.3$, $z = 1-2$.
16. The process of claim 14 wherein the perfluorosulfonic acid membrane is selected from the group consisting of: Nafion® (Du Pont), Dow membrane (Dow Chemical), Flemion membrane (Asahi Glass Co.), Aciplex membrane (Asahi Chem.), BAM (Ballarde), Solvay Hyflon and Gore-select membrane (W.L. Gore, Inc.).
- 20 17. The process of any of claims 9 to 16 wherein the resulting membrane electrode assembly has a zeolite content in the range of 0.1 to 6.0% by weight of the sum of the proton exchange membrane and the monomer of the one or more layers, optionally 0.25 to 0.75%.

18. The process of any of claims 9 to 17 wherein the mixture of the PEM monomer and zeolite is applied to the first electrode by spraying.
19. The process of any of claims 9 to 18 wherein the zeolite is selected from the group consisting of: mordenite, zeolite-A ($\text{Si/Al} \geq 1$), zeolite-Y ($\text{Si/Al} \geq 2.5$), zeolite- β ($\text{Si/Al} \geq 8-20$),
5 ZSM5 ($\text{Si/Al} \geq 10$), Chabazite ($\text{Si/Al} \geq 4$), Clinoptilolite ($\text{Si/Al} \geq 2$) and Faujasite ($\text{Si/Al} \geq 1.5$).
20. A membrane electrode assembly obtainable by the process of any of claims 9 to 19.

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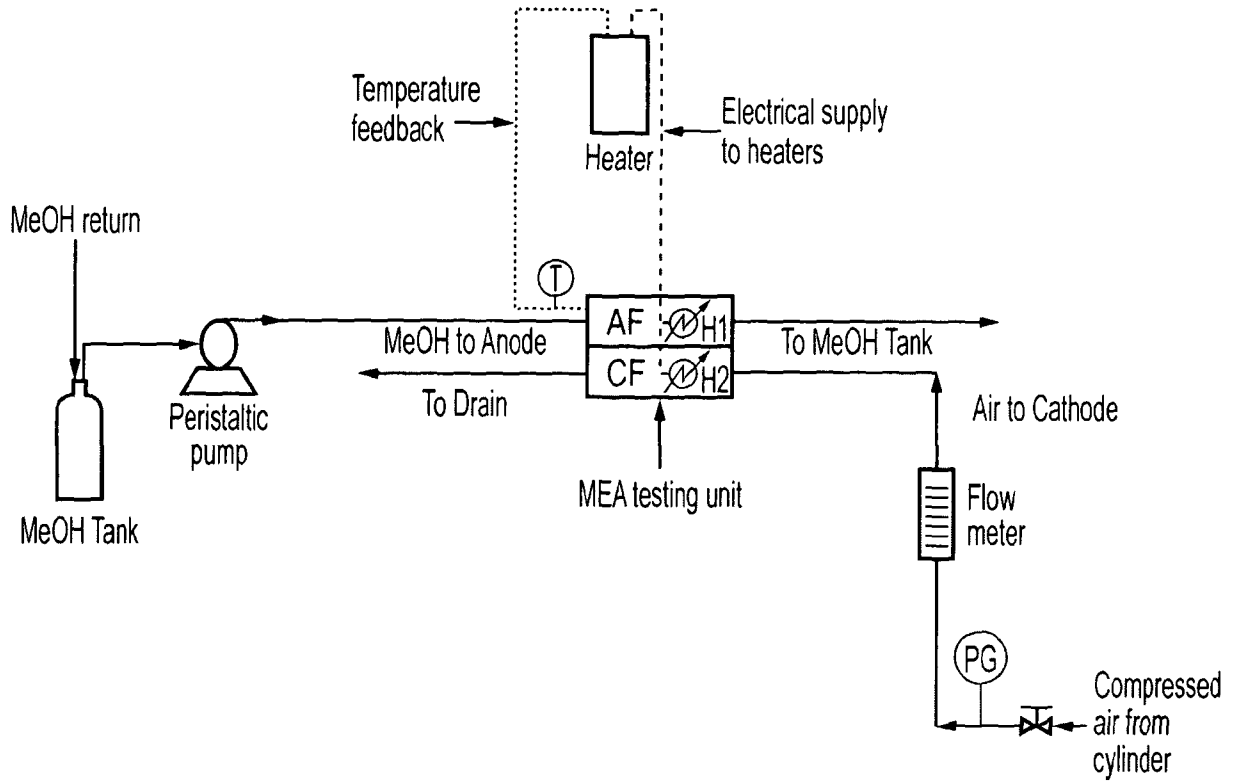


FIG. 1

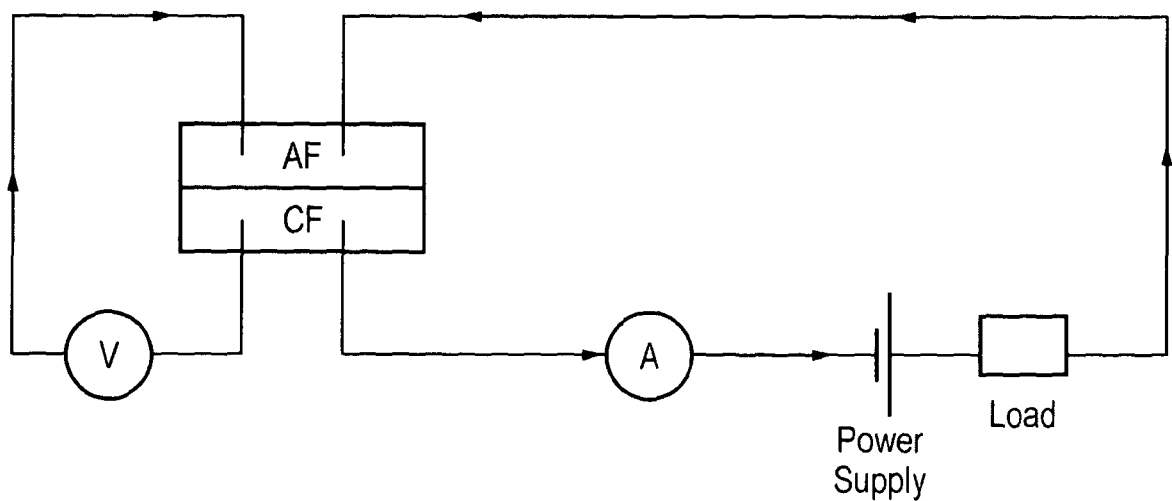


FIG. 2

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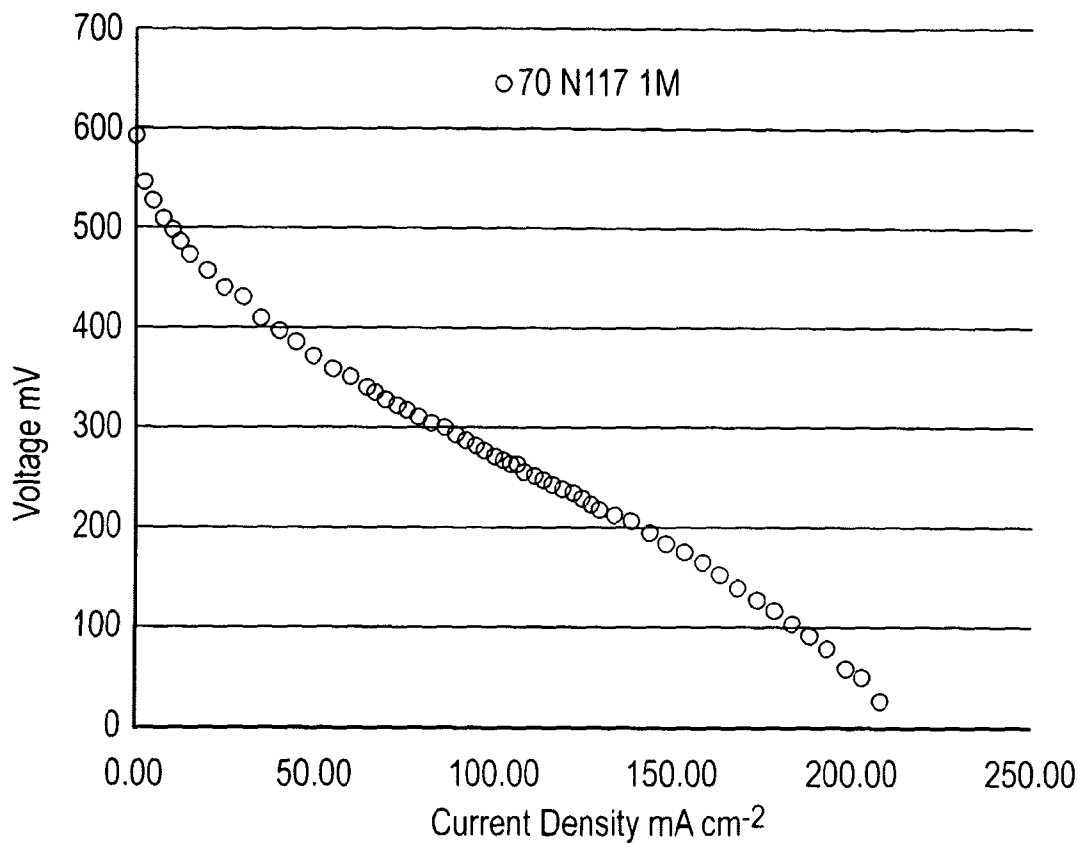


FIG. 3

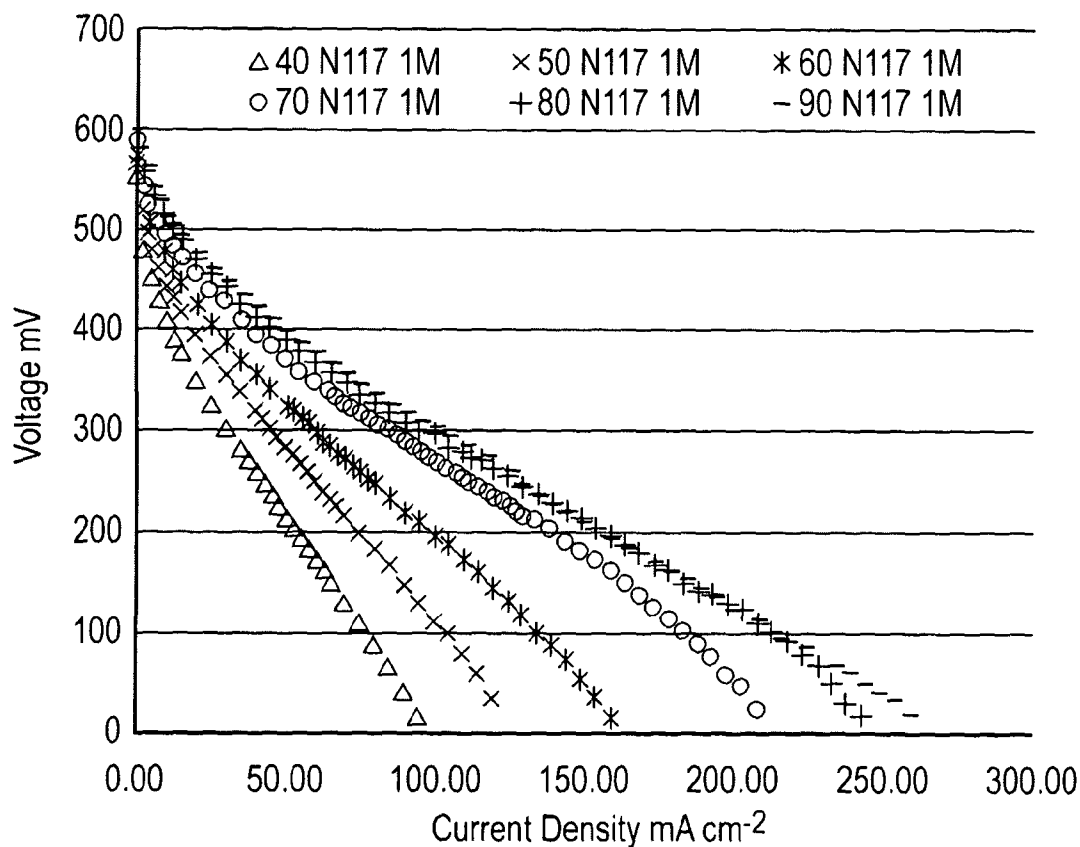


FIG. 4

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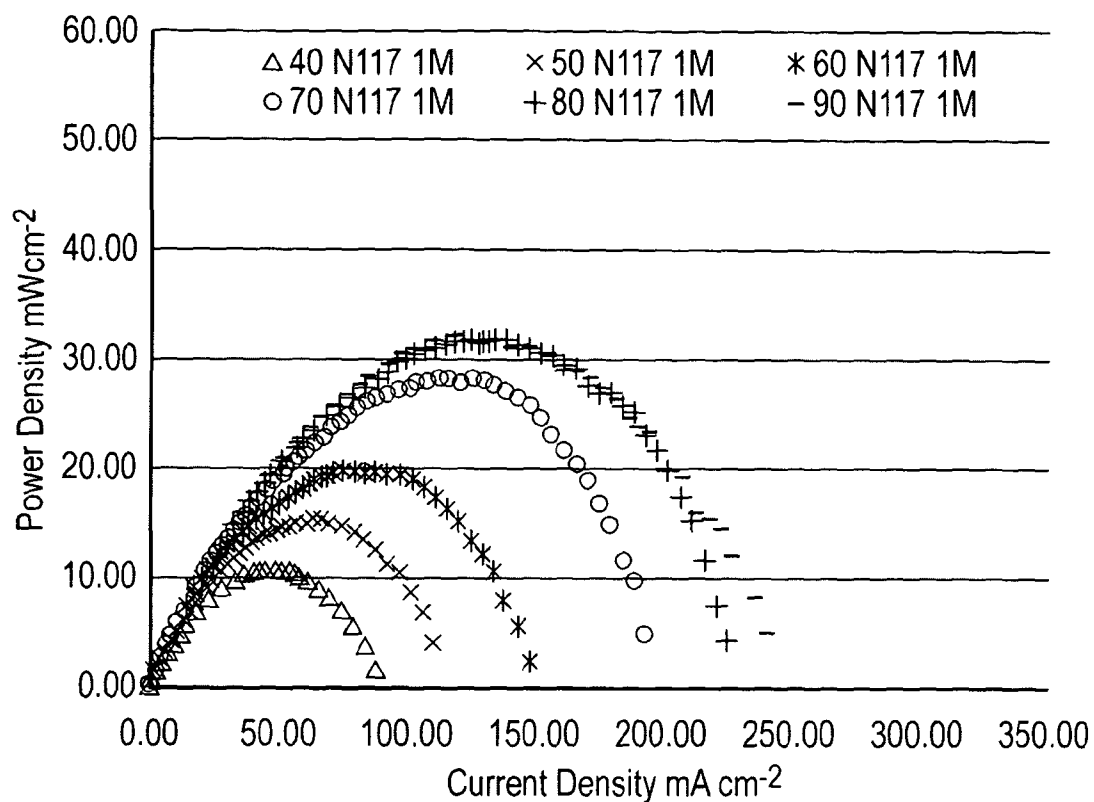


FIG. 5

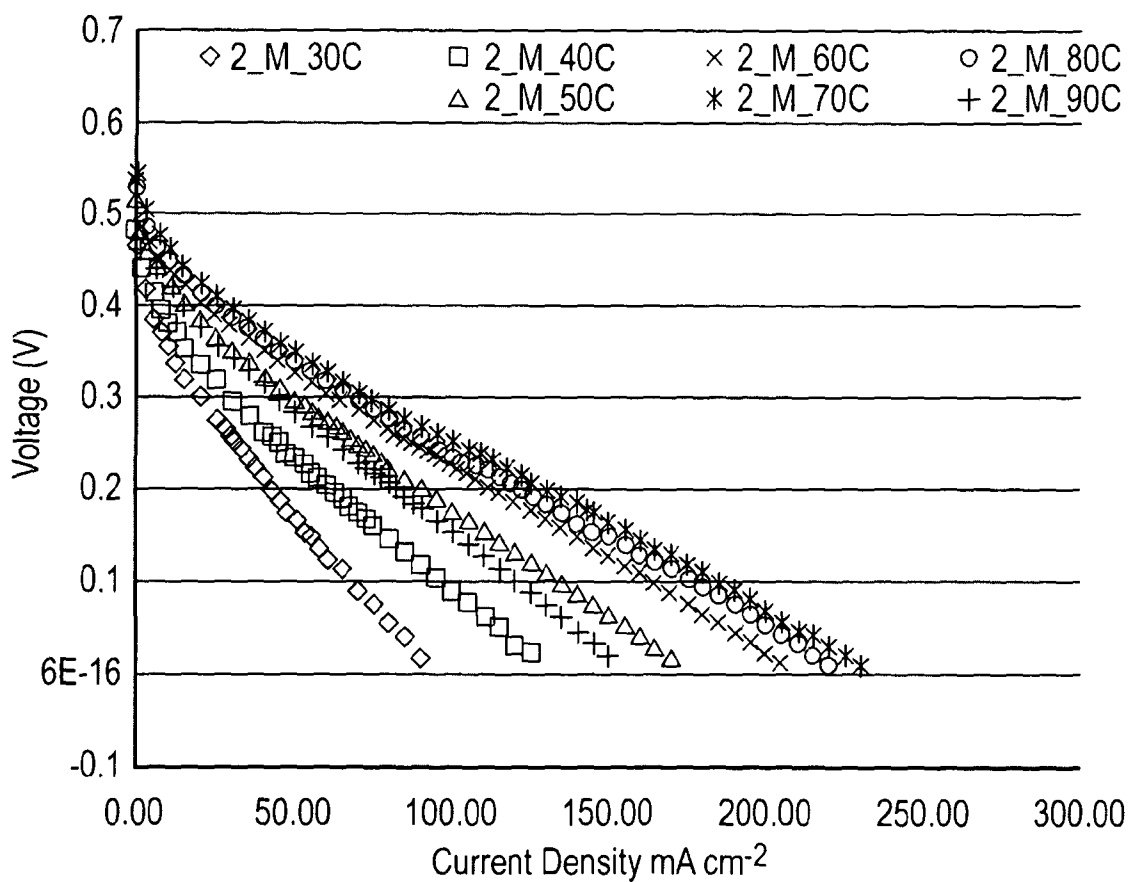


FIG. 6

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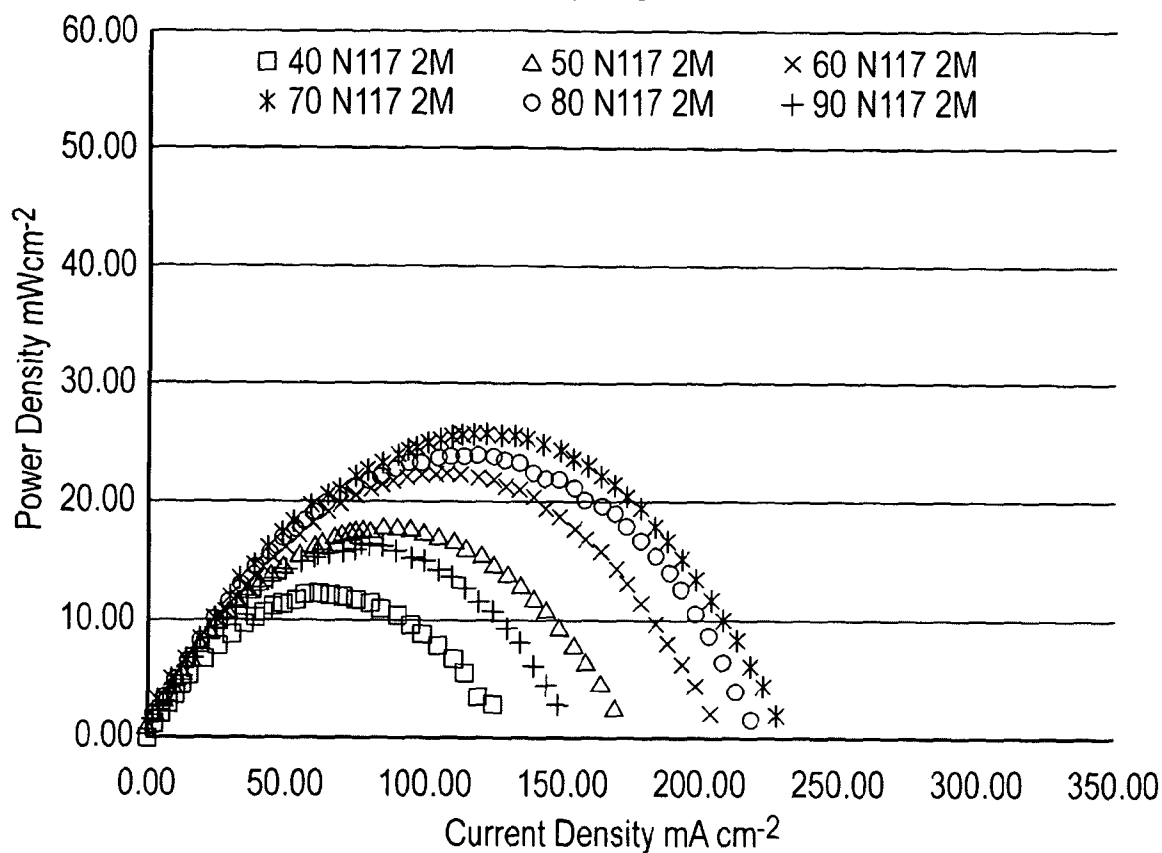


FIG. 7

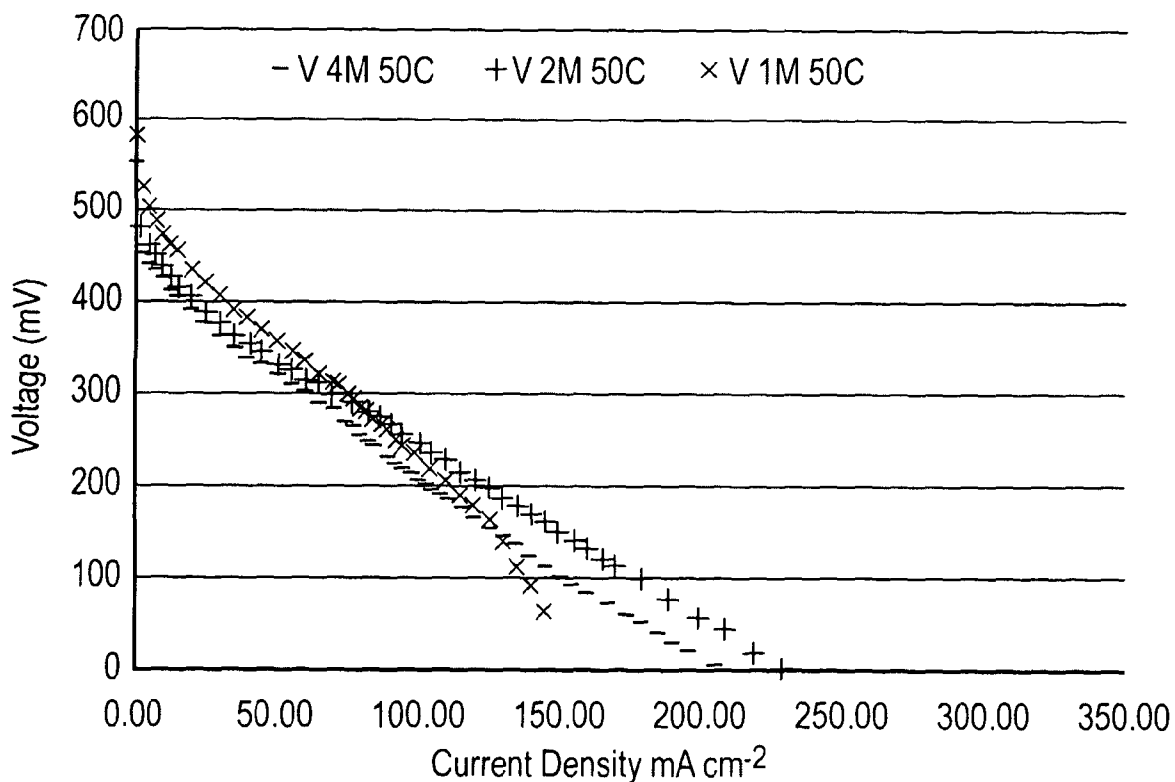


FIG. 8

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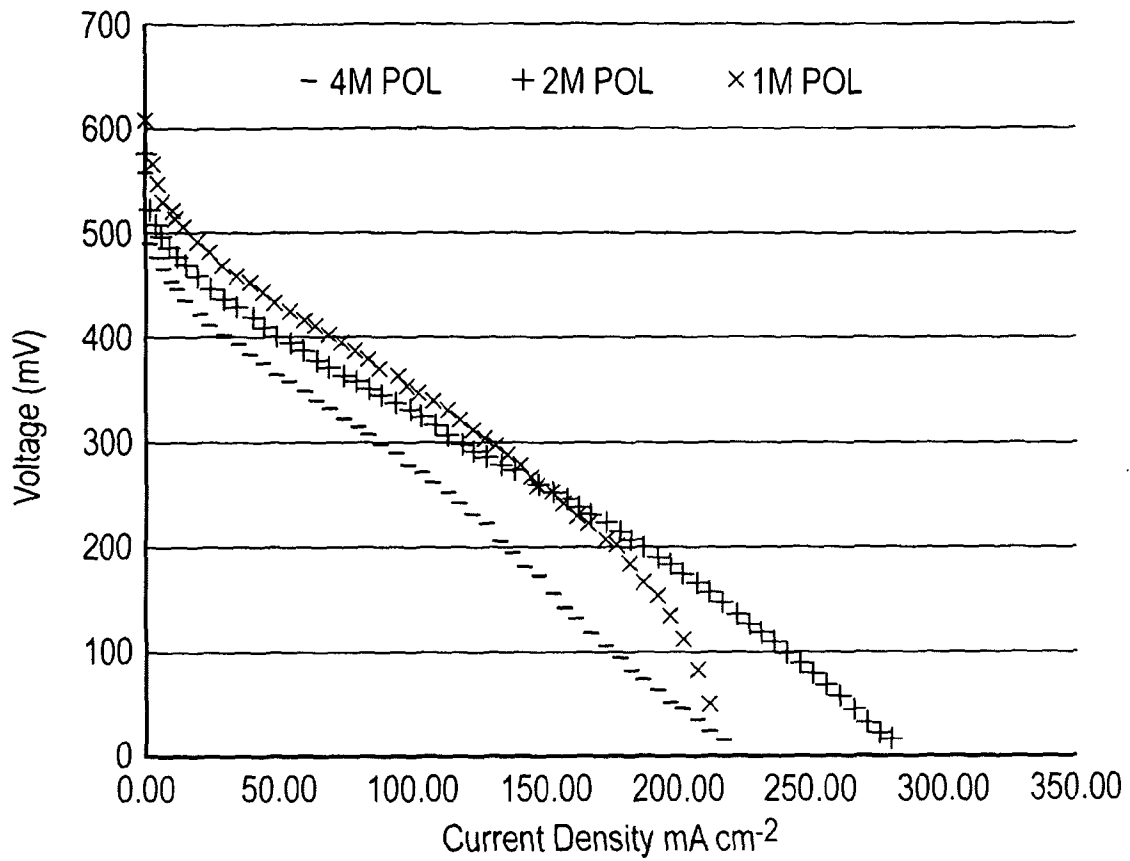


FIG. 9

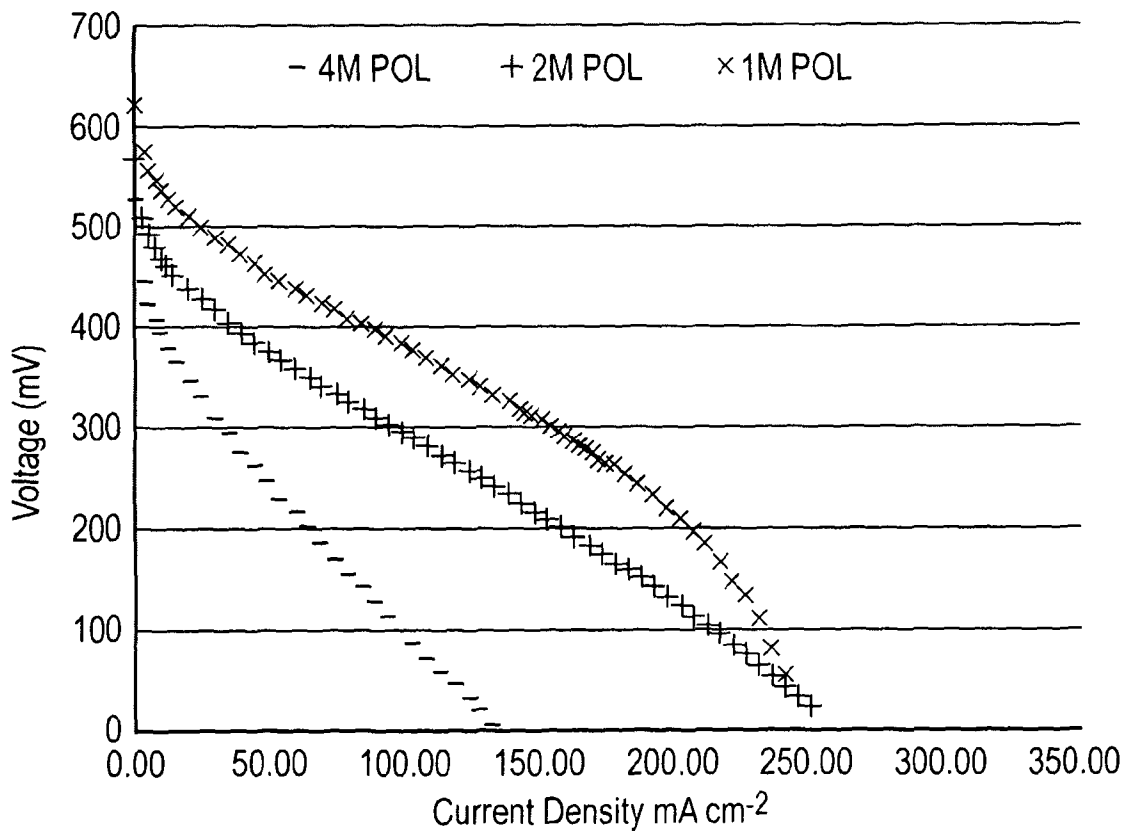


FIG. 10

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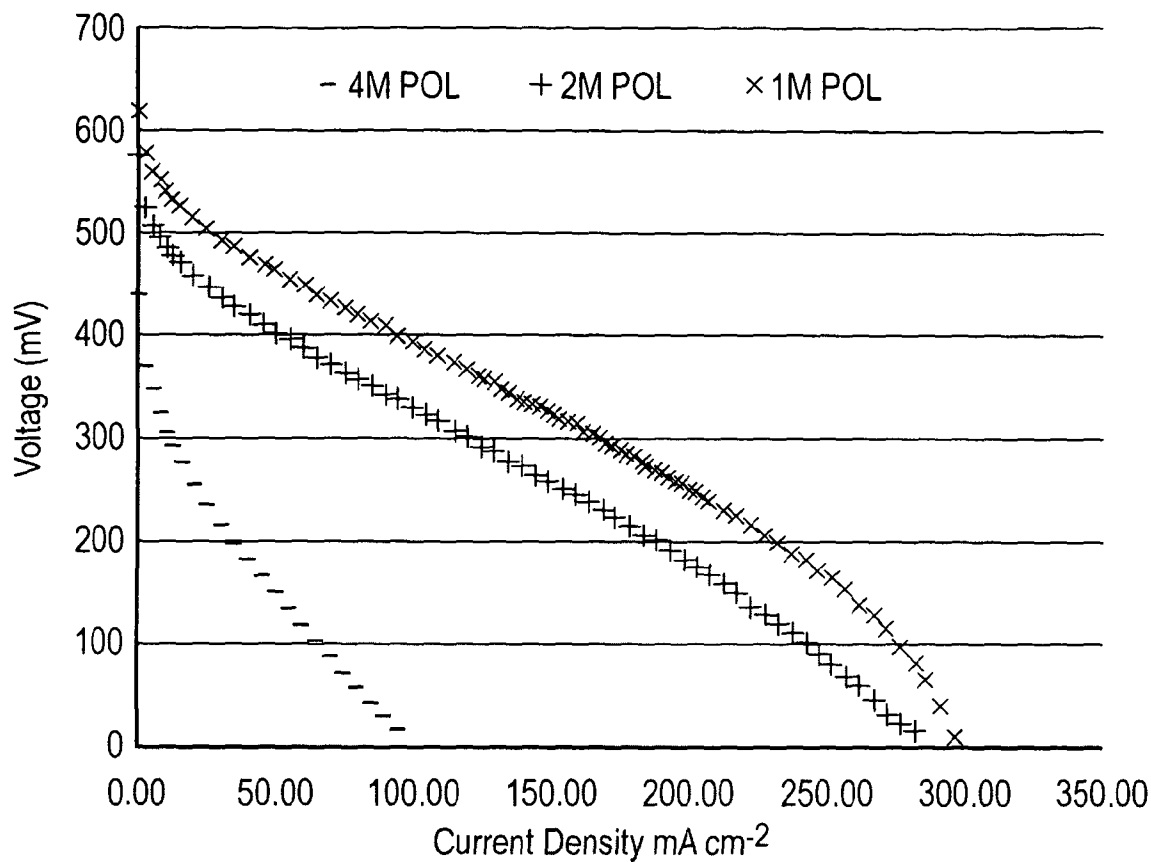


FIG. 11

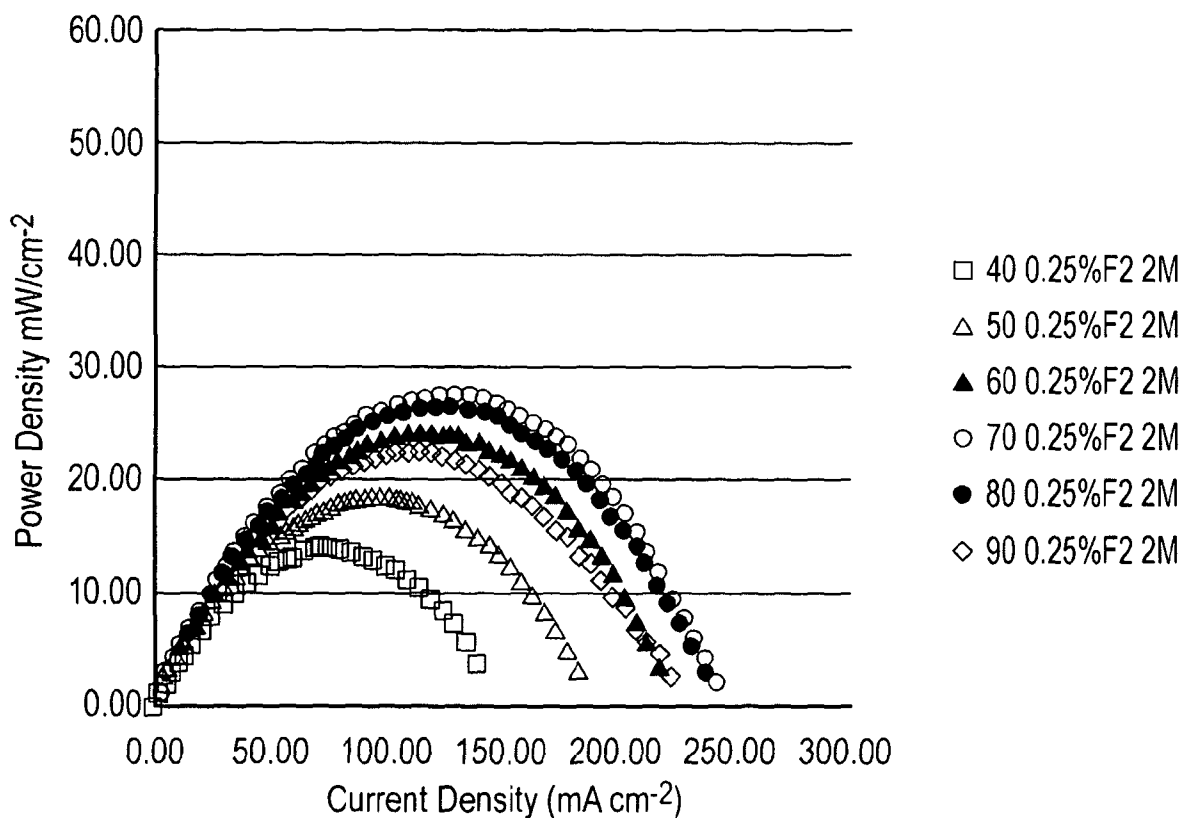


FIG. 12

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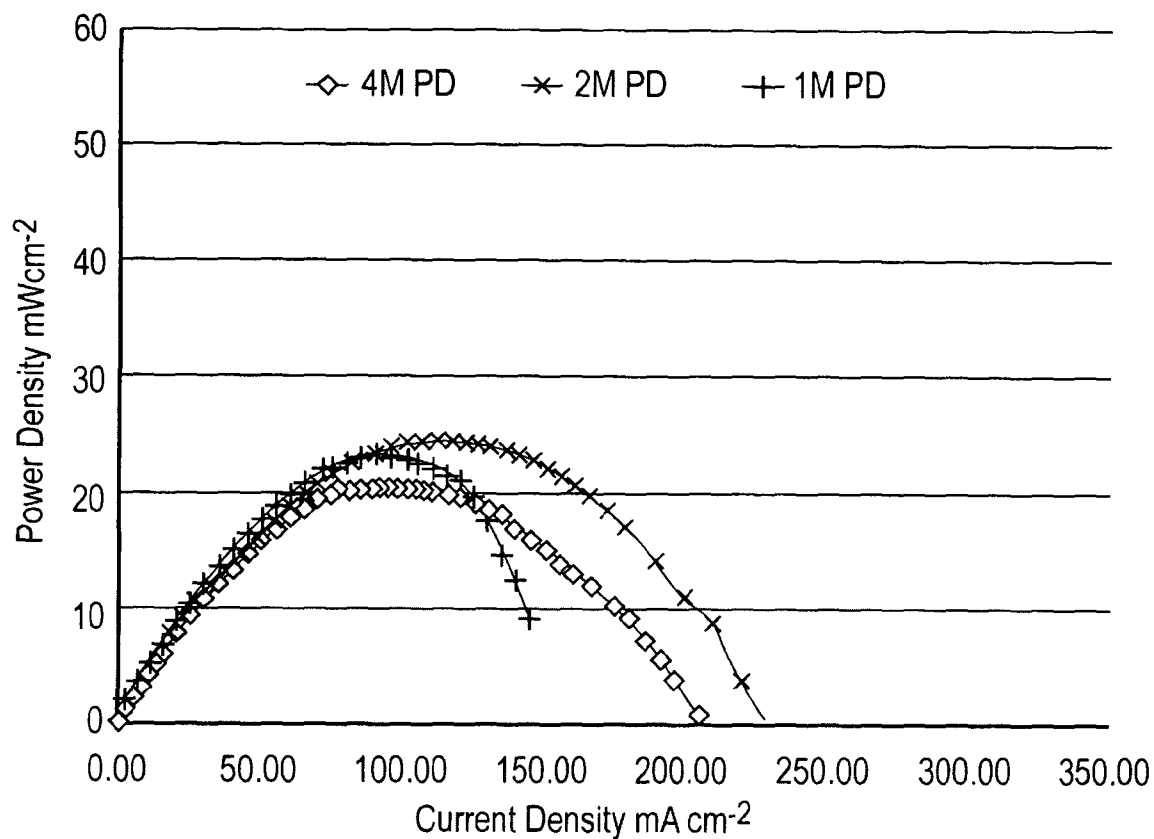


FIG. 13

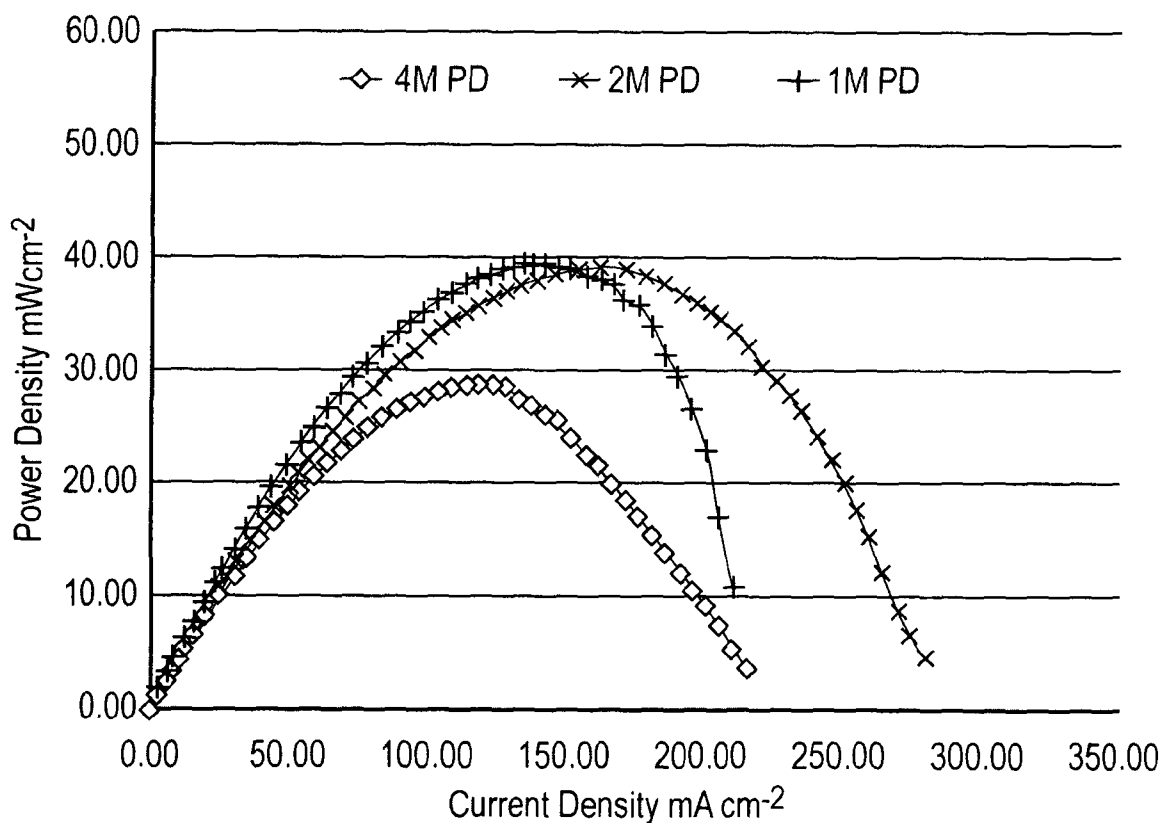


FIG. 14

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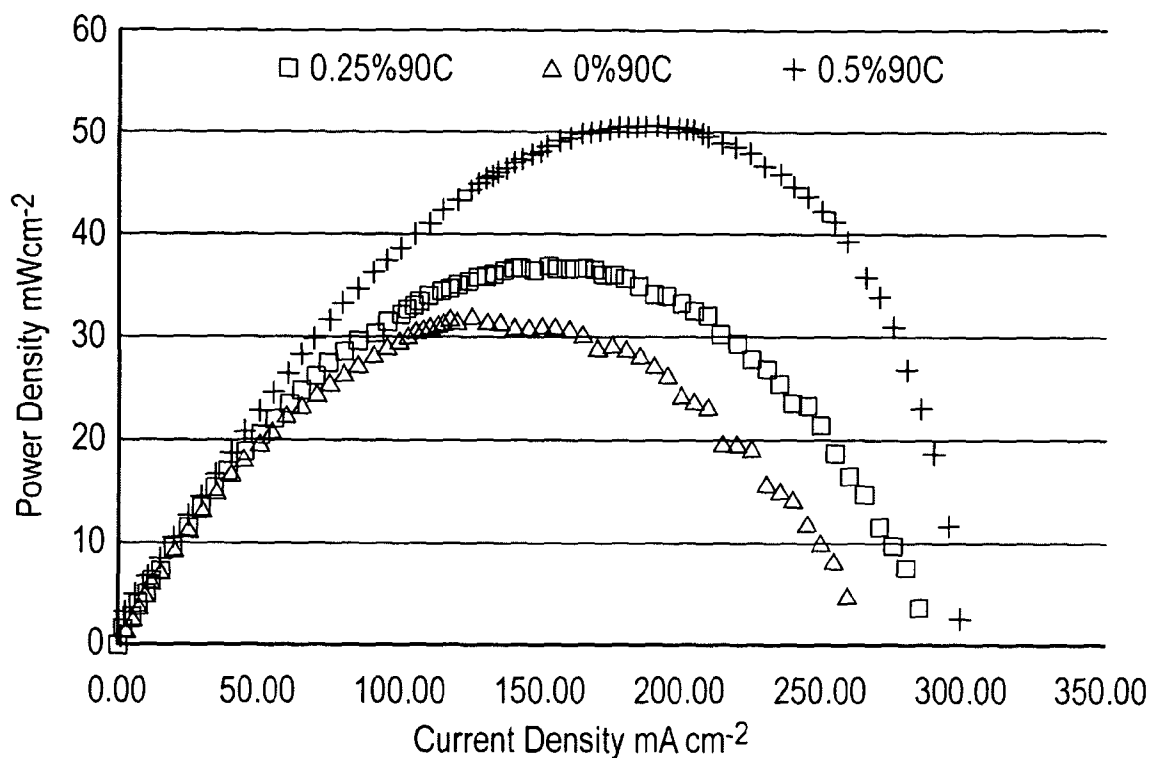


FIG. 15

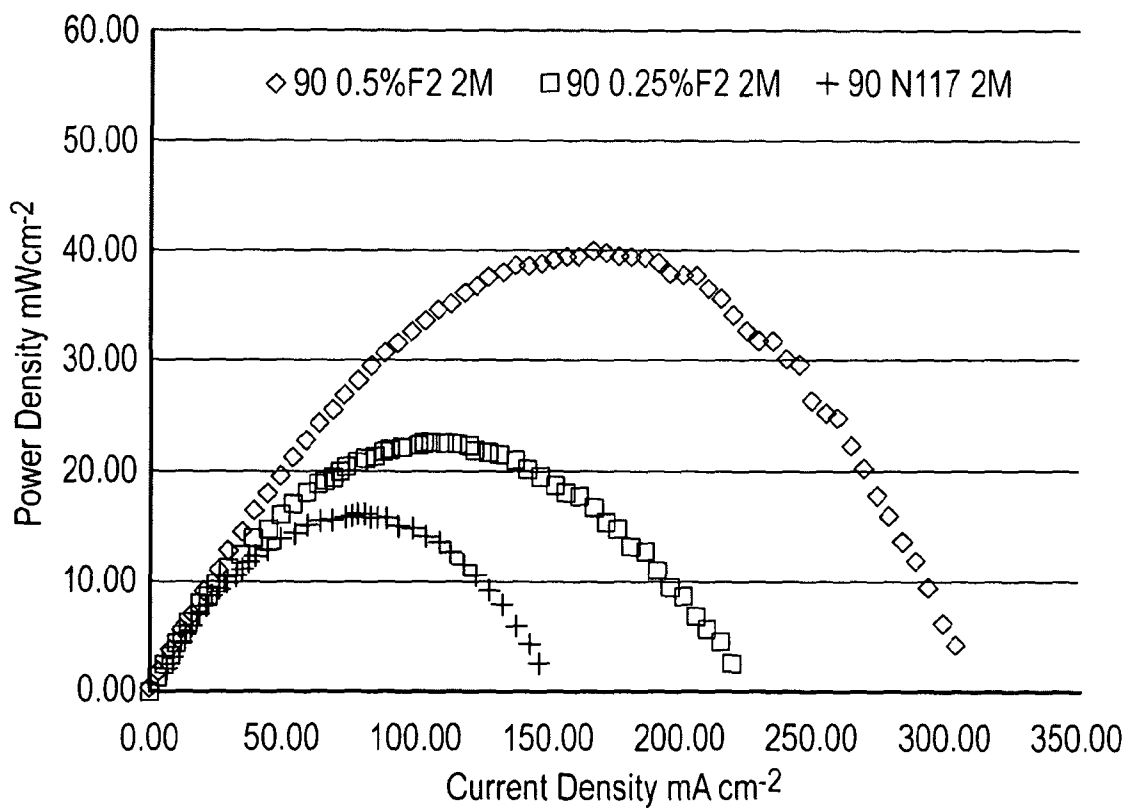


FIG. 16

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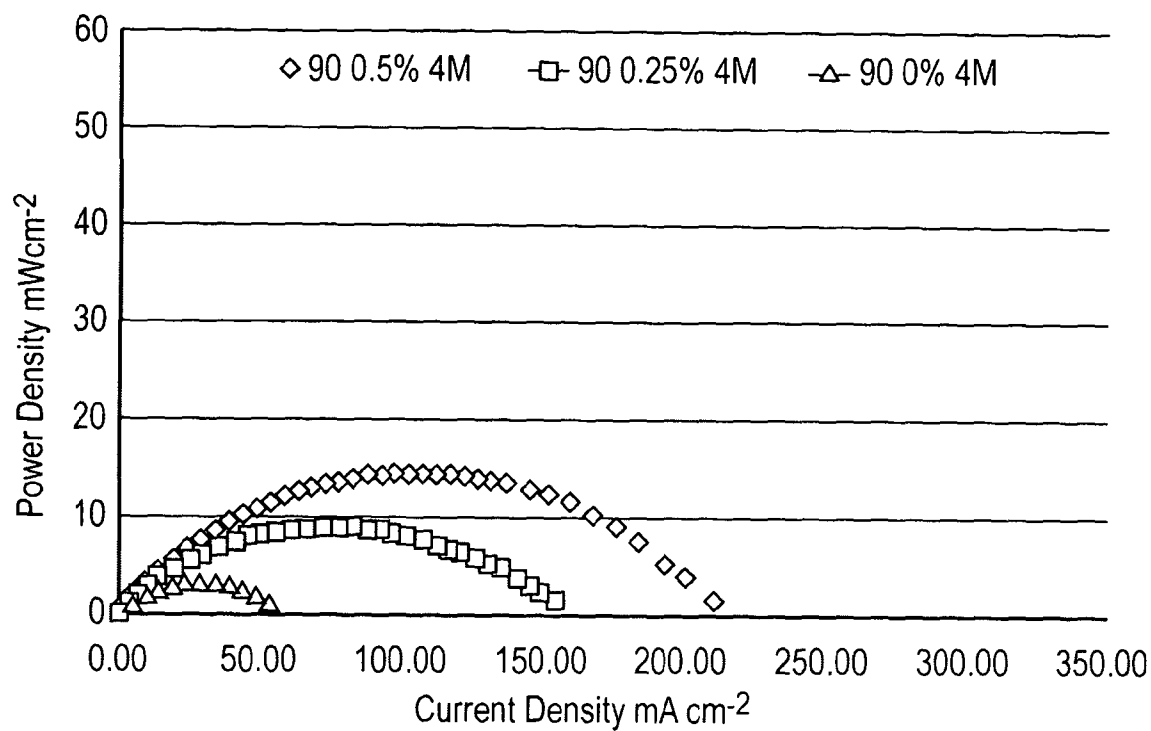


FIG. 17

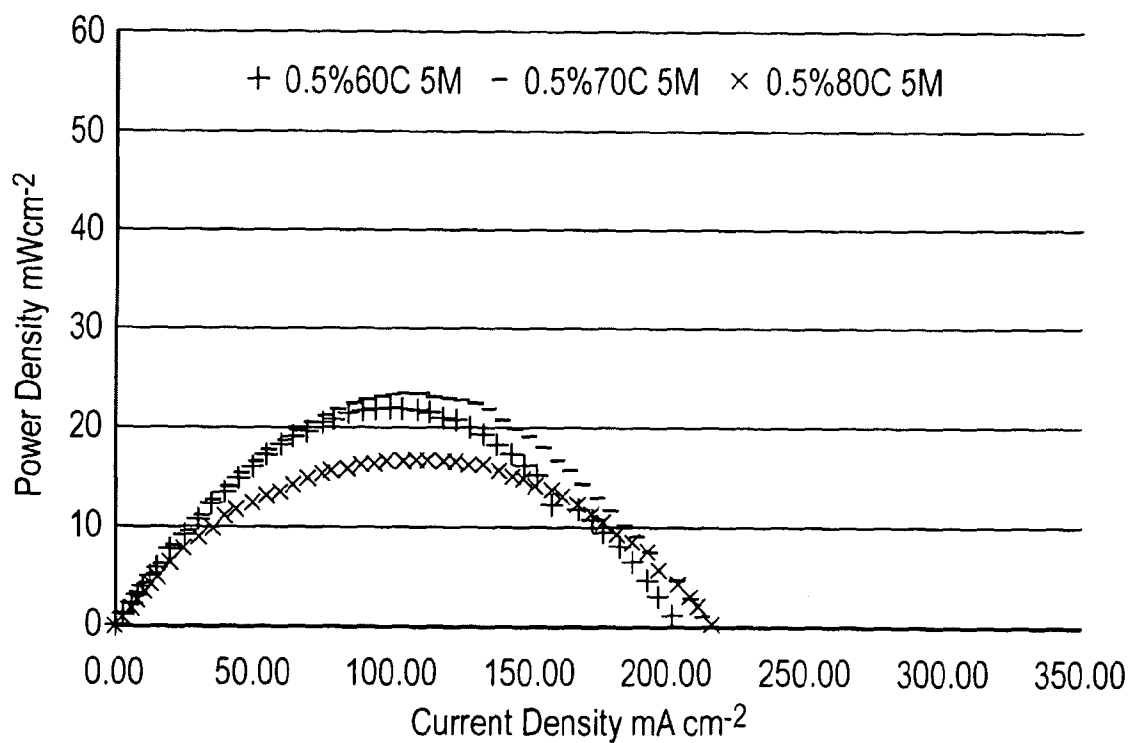


FIG. 18

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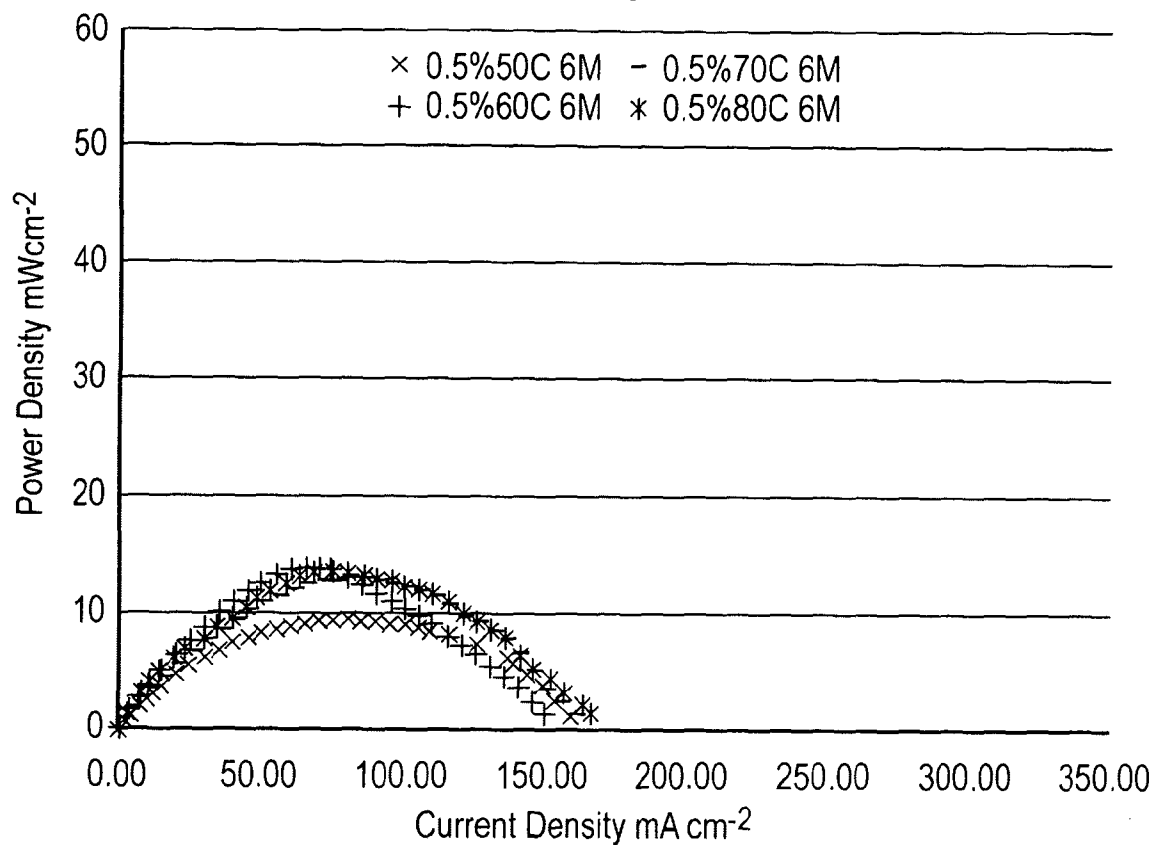


FIG. 19

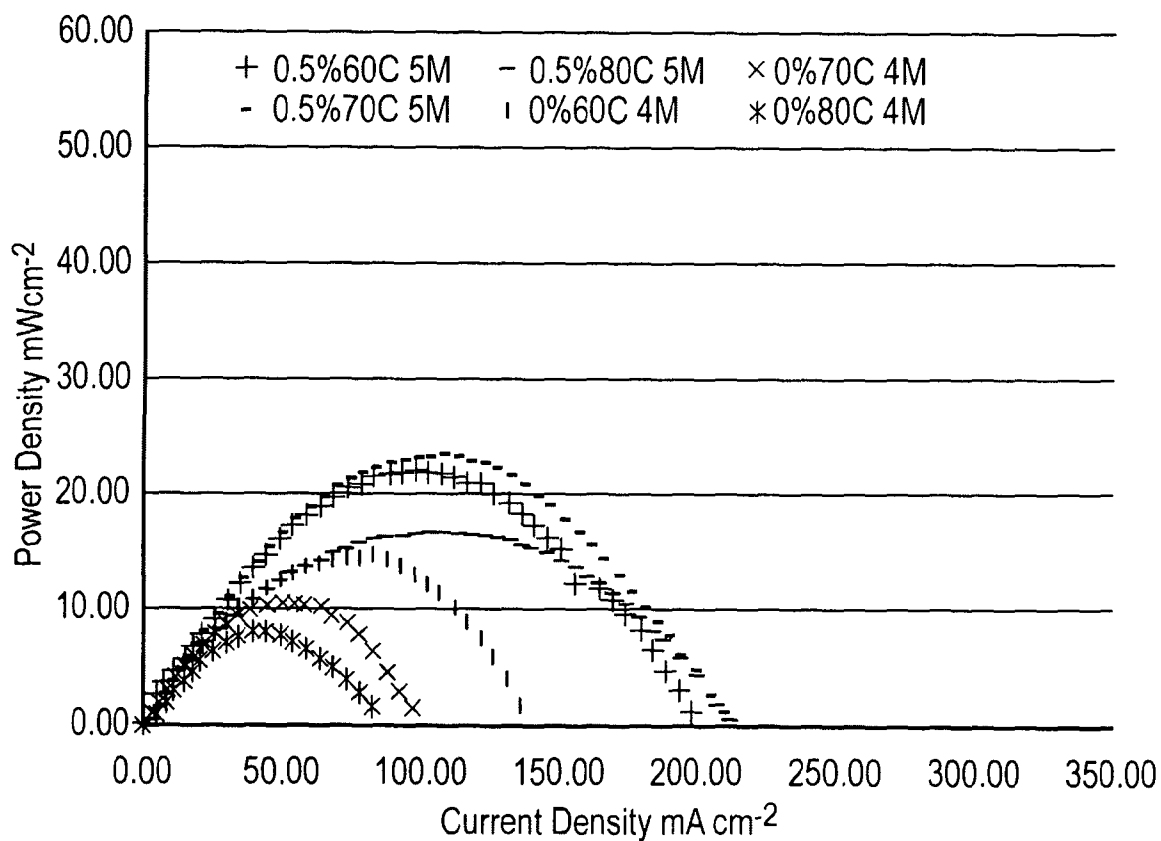


FIG. 20

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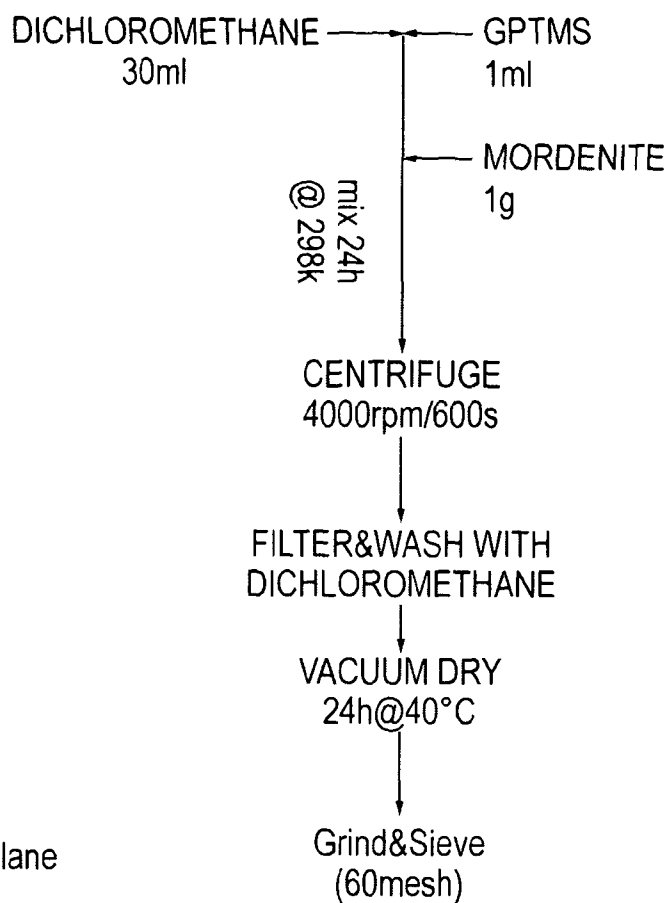


FIG. 21

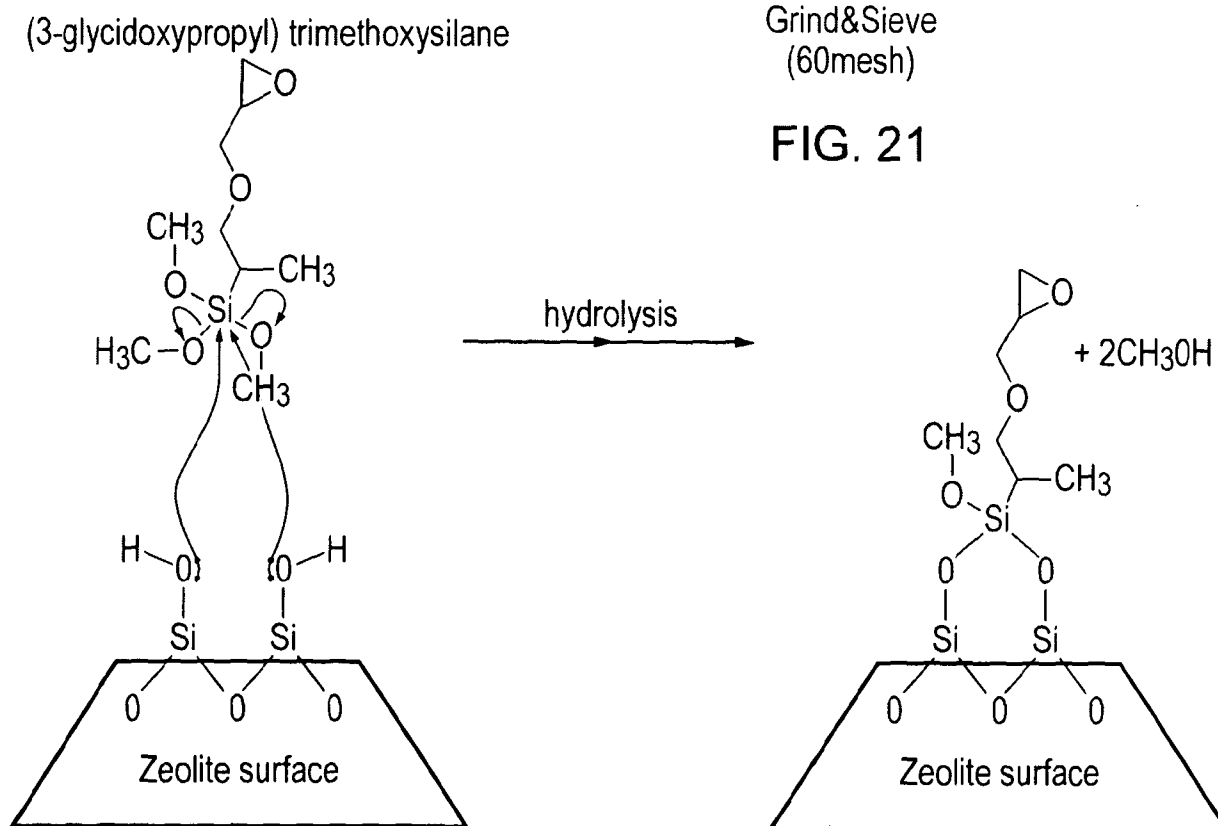


FIG. 22

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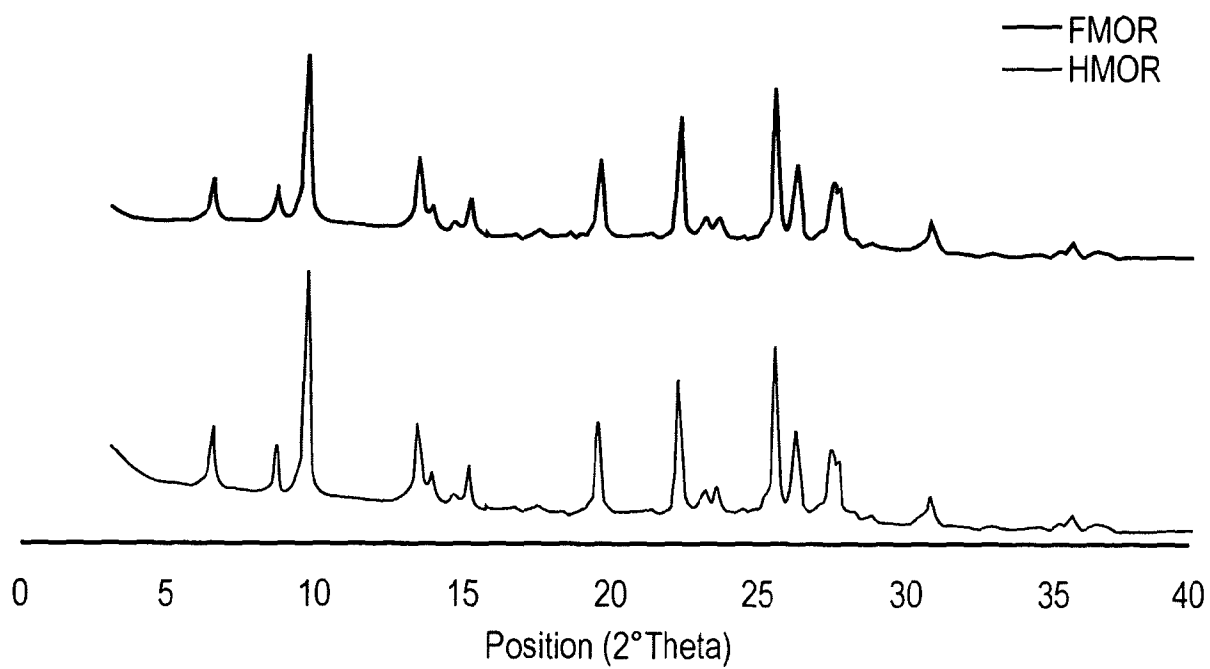


FIG. 23

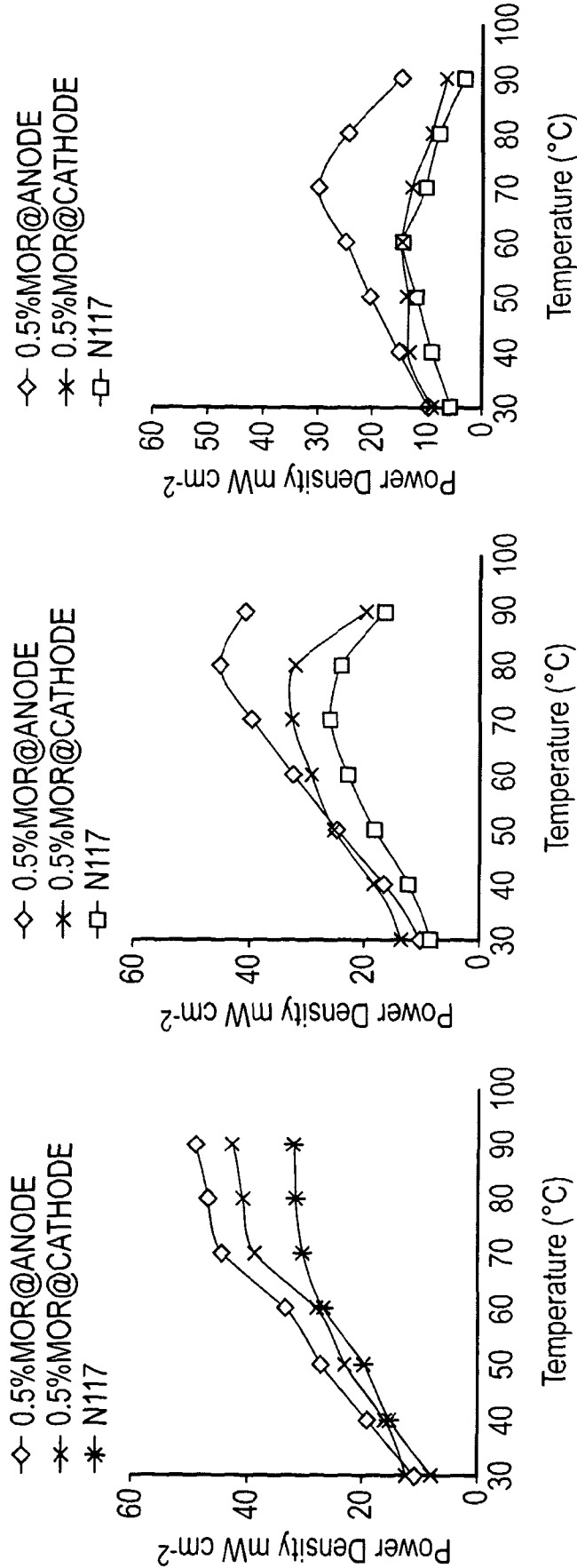


FIG. 24(c)

FIG. 24(b)

FIG. 24(a)

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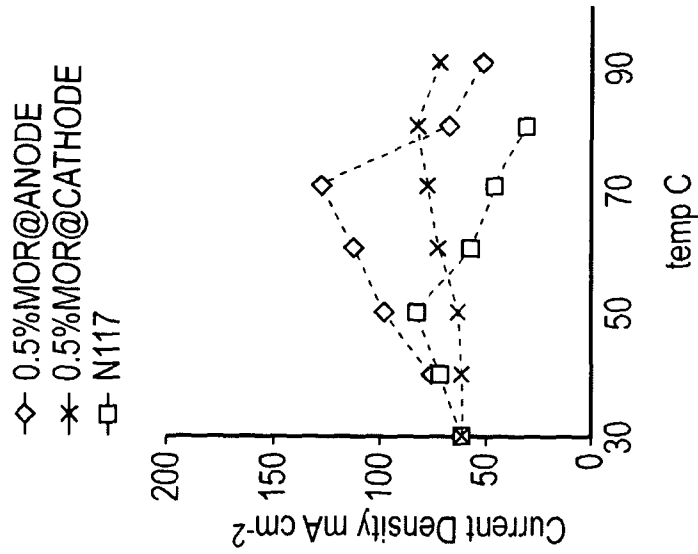


FIG. 25(c)

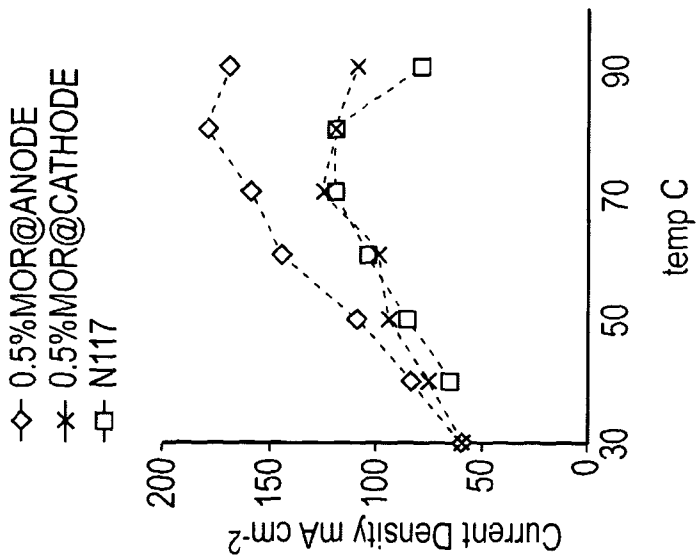


FIG. 25(b)

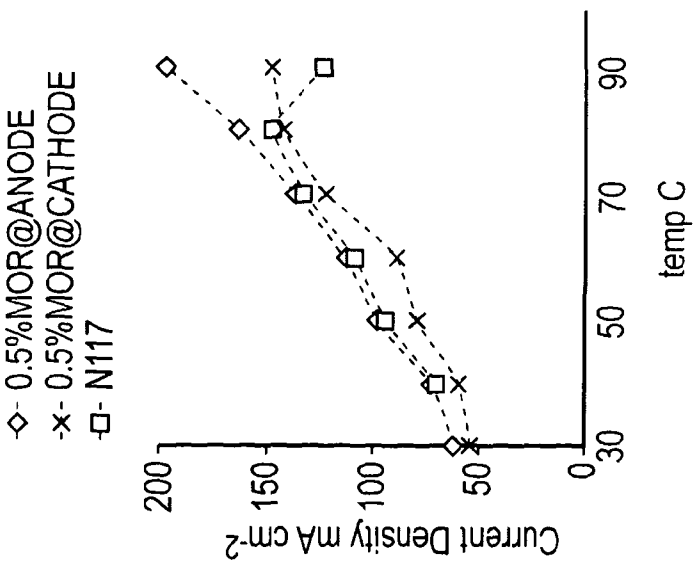


FIG. 25(a)

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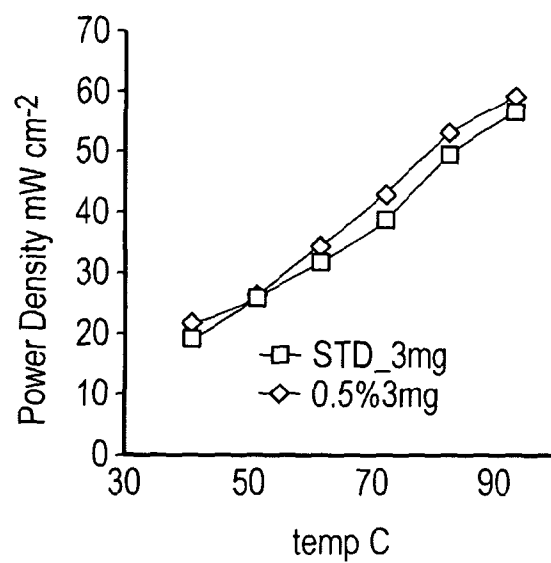


FIG. 26(a)

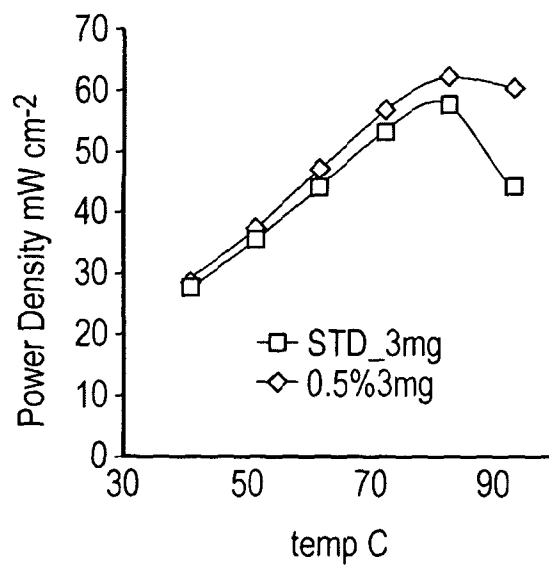


FIG. 26(b)

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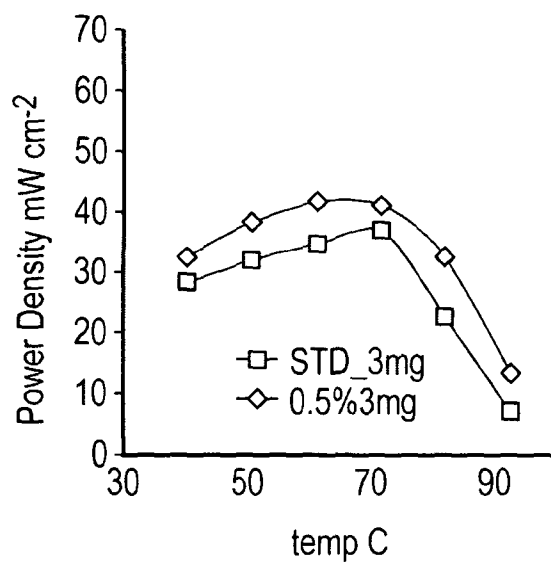


FIG. 26(c)

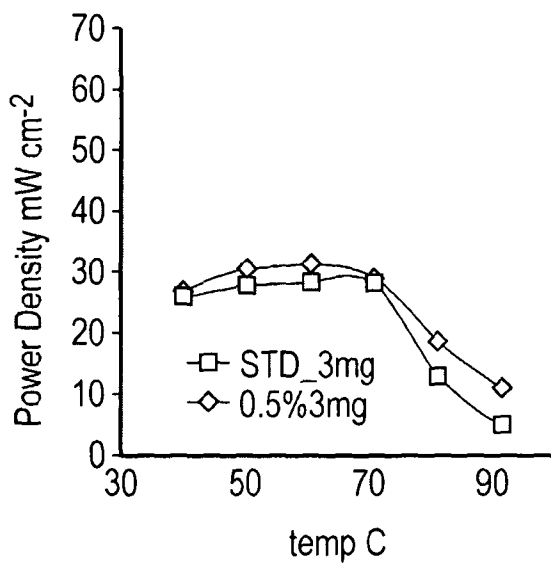


FIG. 26(d)

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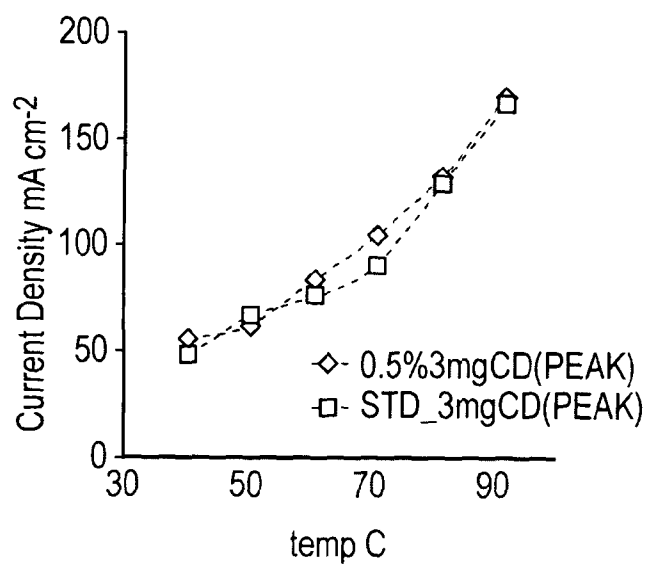


FIG. 27(a)

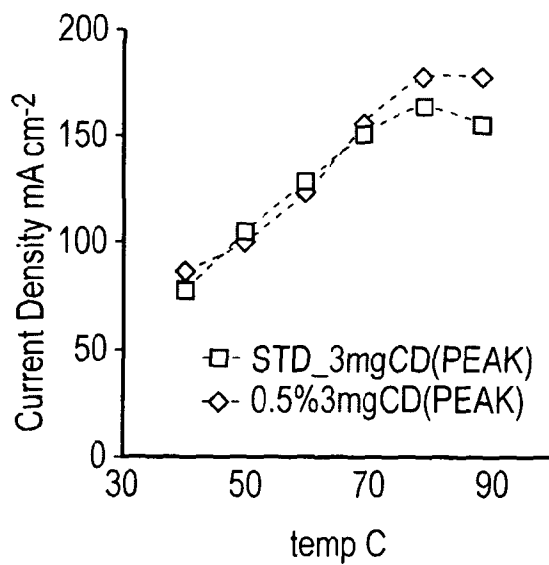


FIG. 27(b)

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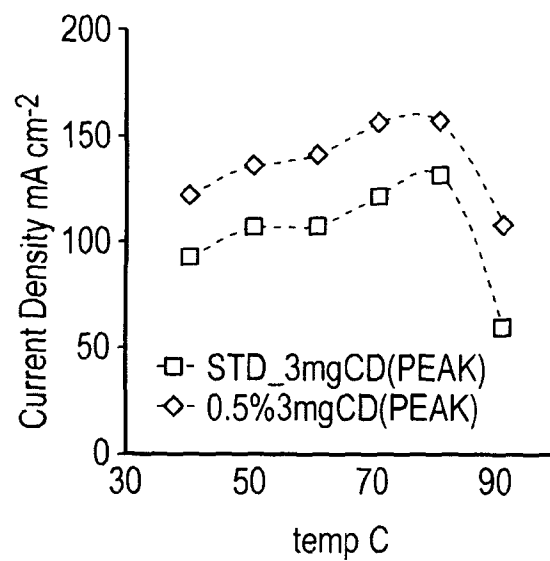


FIG. 27(c)

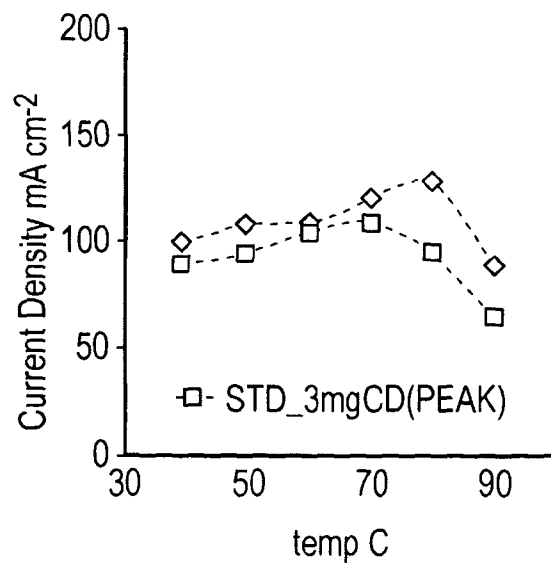


FIG. 27(d)

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- 3-LAYER 0.375%(CAL)
- △ 4-LAYER 0.5%(CD)
- ◇ 7-LAYER 0.5%(CAL)
- × 5-LAYER 0.63%(AG)

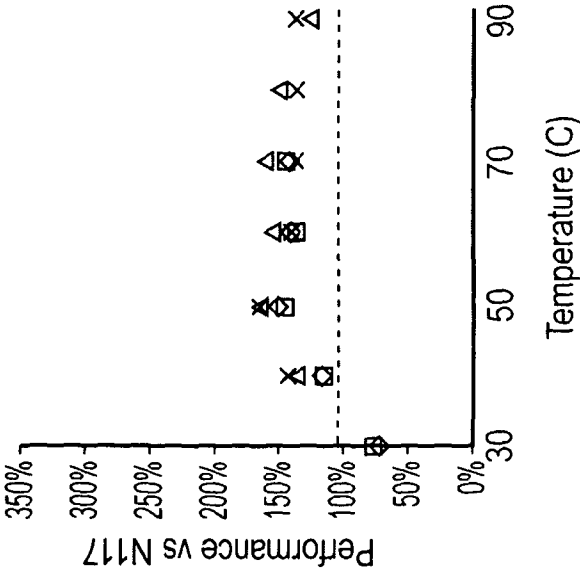


FIG. 28(a1)

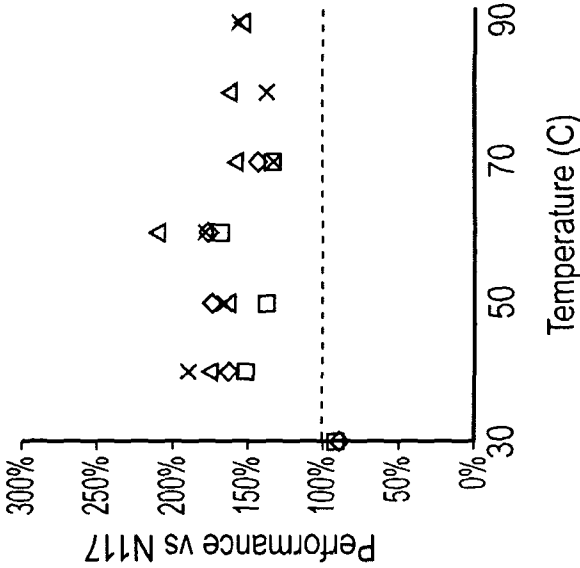


FIG. 28(a2)

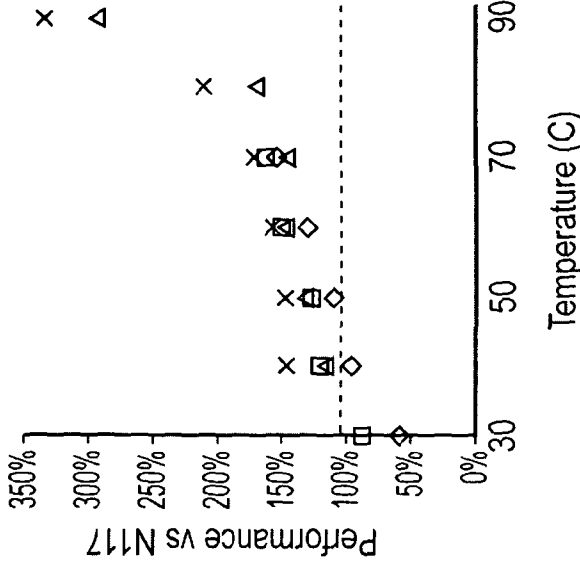


FIG. 28(b1)

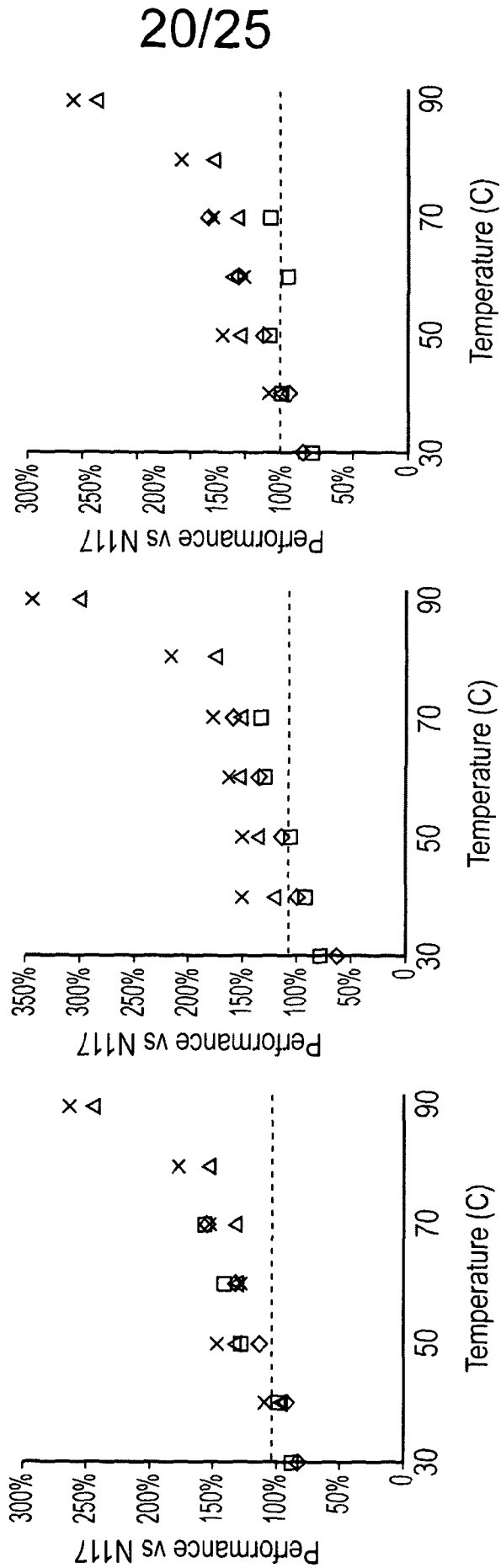


FIG. 28(c2)

FIG. 28(c1)

FIG. 28(b2)

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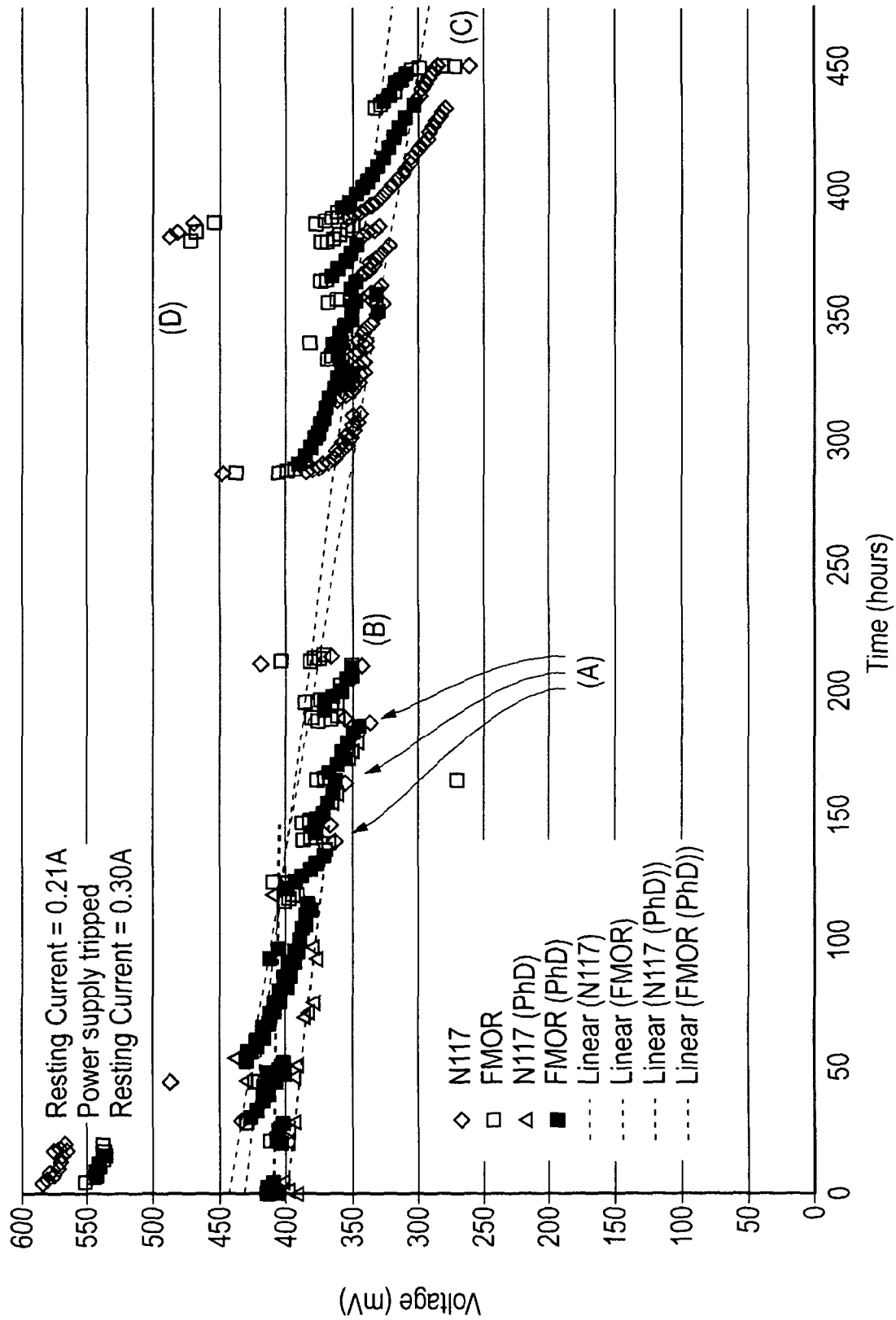


FIG. 29

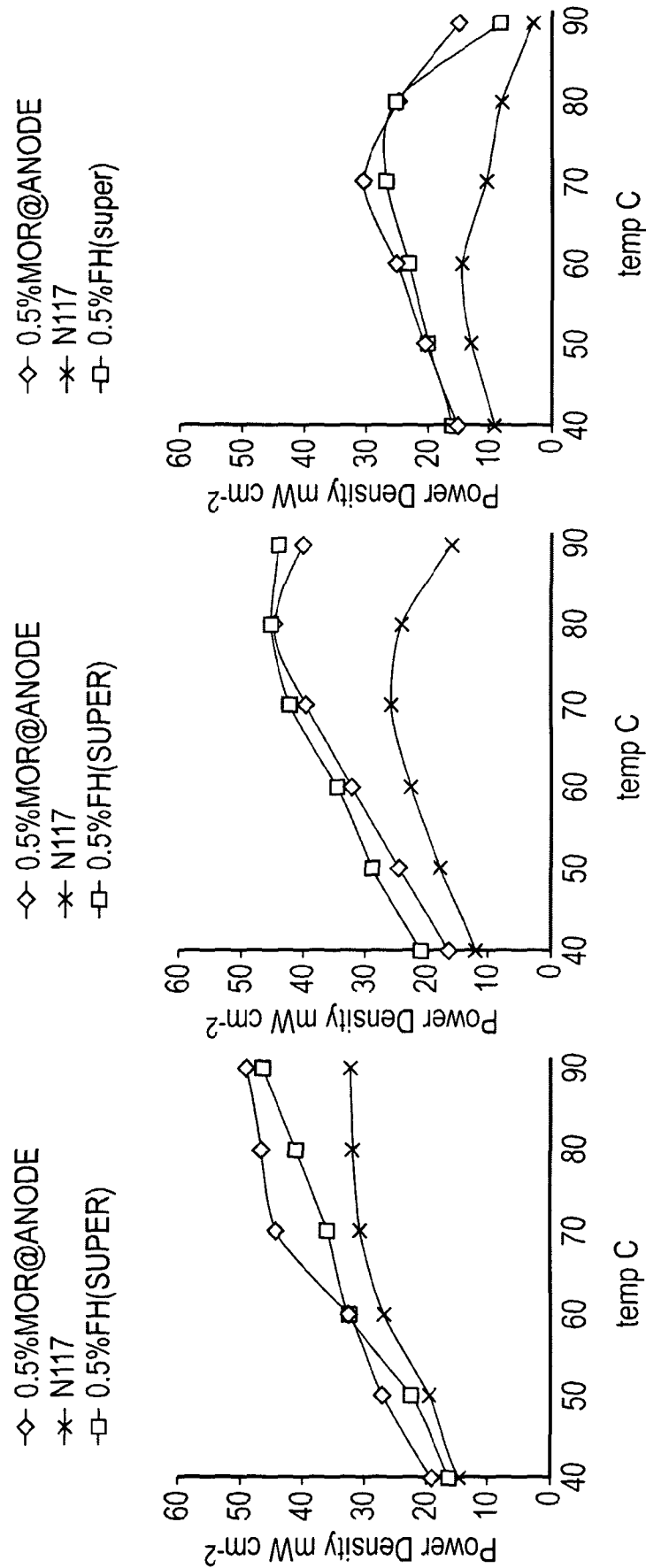


FIG. 30(c)

FIG. 30(b)

FIG. 30(a)

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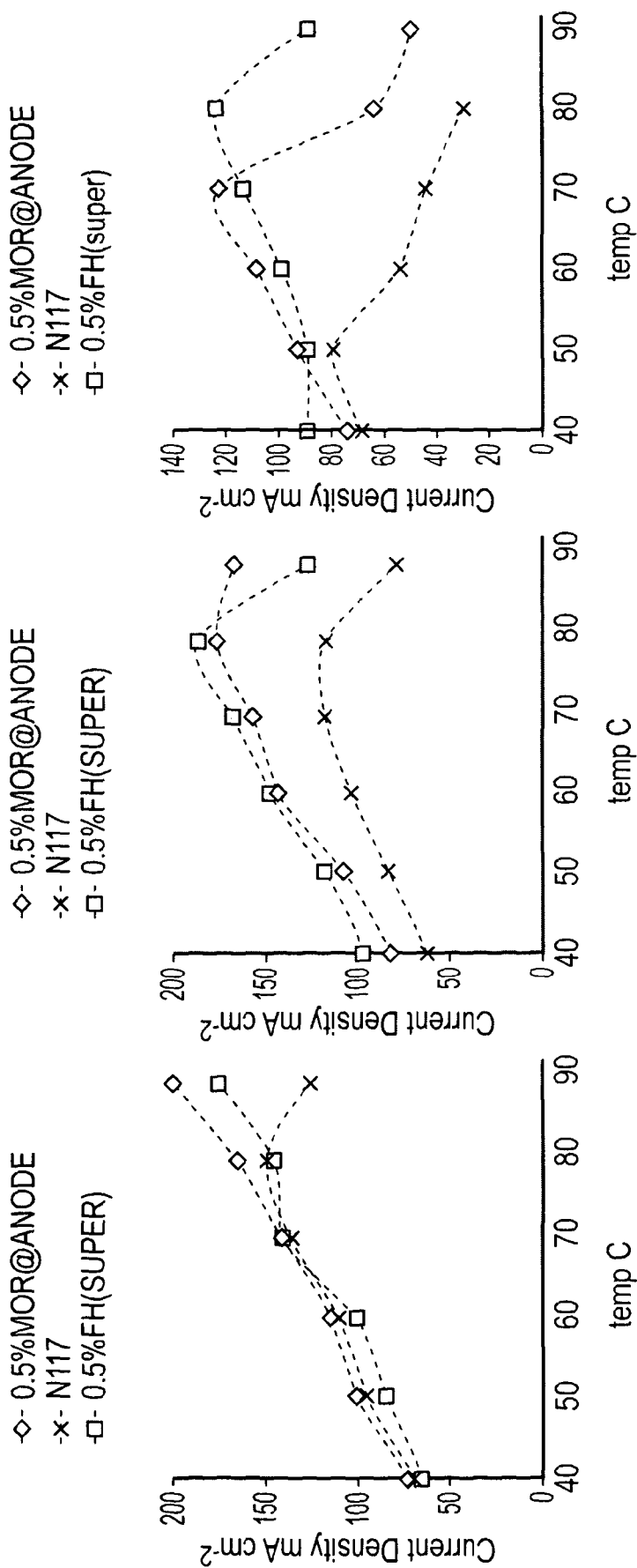


FIG. 31(c)

FIG. 31(b)

FIG. 31(a)

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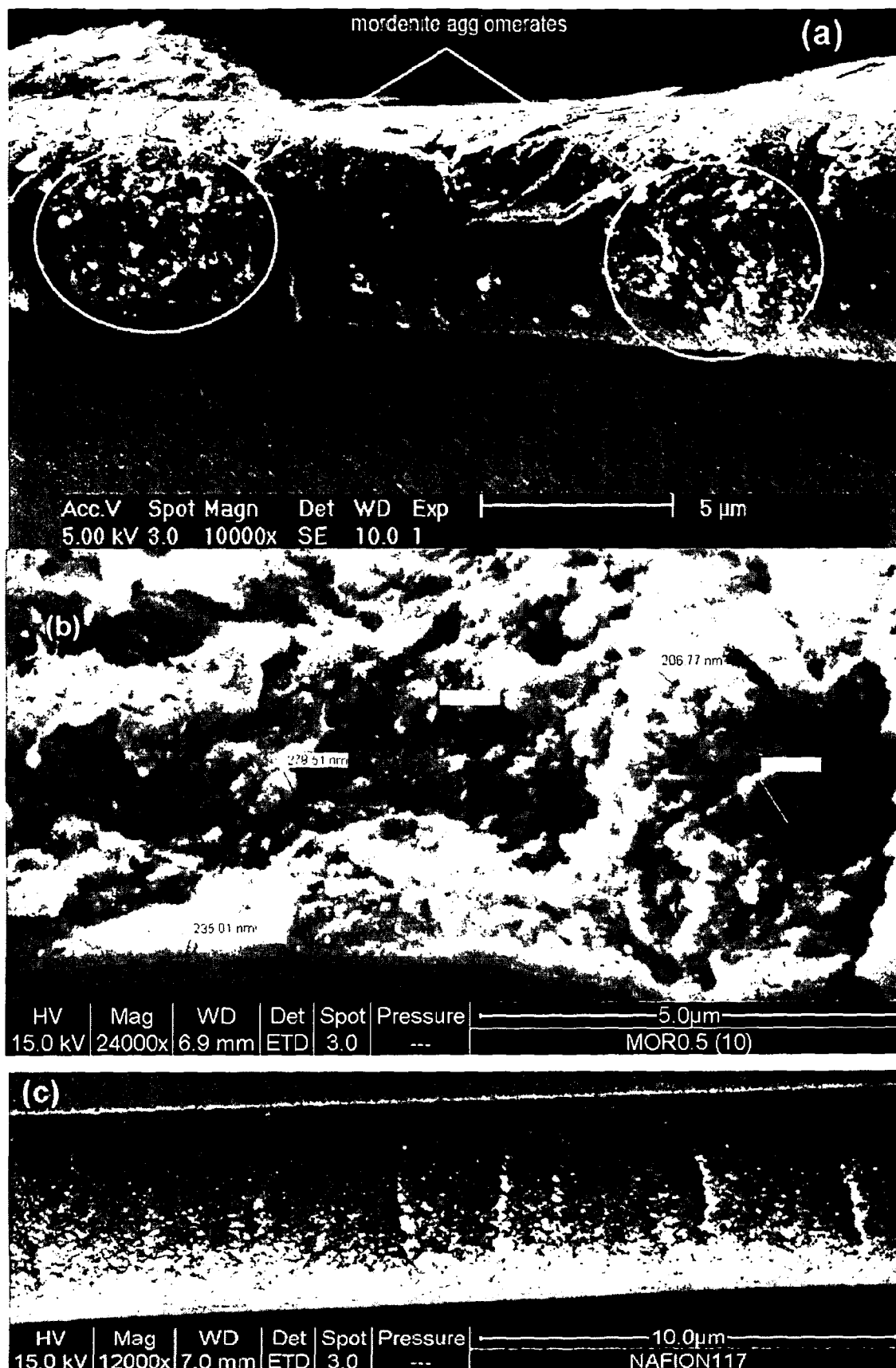


FIG. 32

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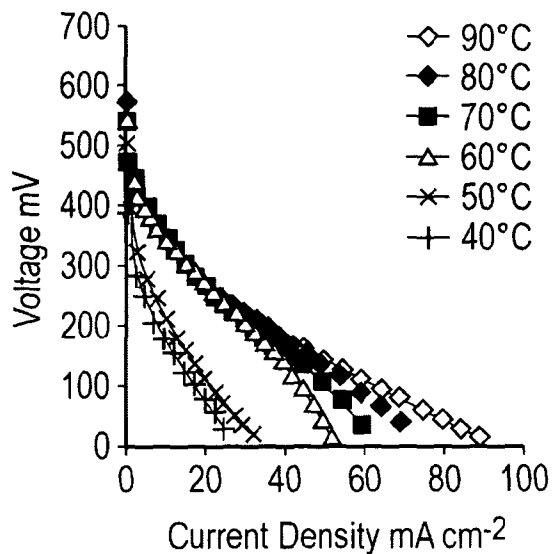


FIG. 33(a1)

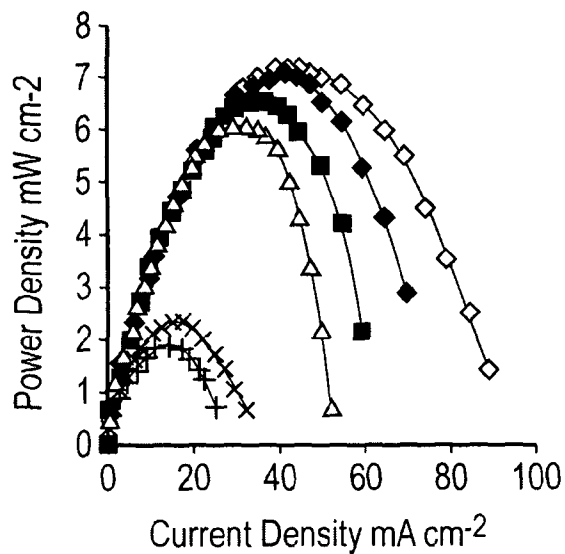


FIG. 33(a2)

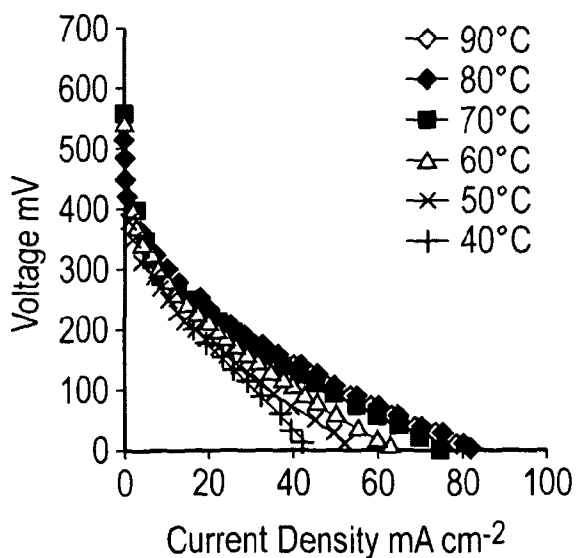


FIG. 33(b1)

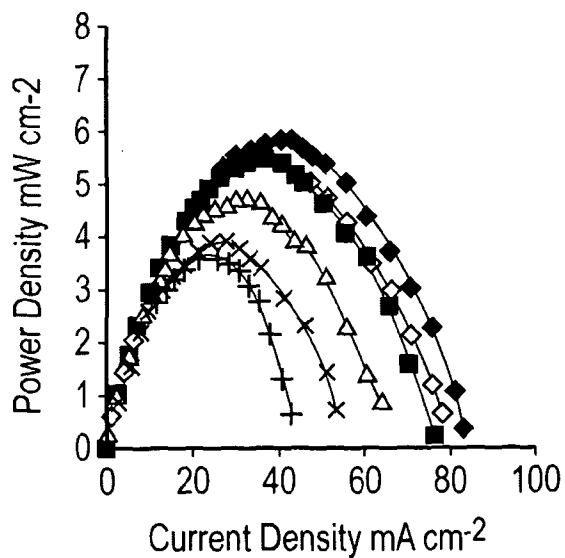


FIG. 33(b2)

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/051531

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TRICOLI V ET AL: "Zeolite-Nafion composites as ion conducting membrane materials", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 48, no. 18, 1 August 2003 (2003-08-01), pages 2625-2633, XP004435009, ISSN: 0013-4686, DOI: 10.1016/S0013-4686(03)00306-2 the whole document * see p.2625, right col. - p.2626, right col.; p.2633, Concluding remarks * ----- -/--	1-20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

13 December 2011

Date of mailing of the international search report

28/12/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3016

Authorized officer

Stellmach, Joachim

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/051531

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/030198 A1 (UNIV NANYANG [SG]; GASHUB TECHNOLOGY PTE LTD [SG]; HAN MING [SG]; CHAN) 13 March 2008 (2008-03-13) the whole document * see [0022] - [0026]; [0049] - [0060]; especially claim 11, all claims *	1-20
X	EP 1 648 047 A1 (SAMSUNG SDI CO LTD [KR]) 19 April 2006 (2006-04-19) the whole document * see [0041] - [0057]; claims *	1-20
Y	US 2004/241520 A1 (HA HEUNG-YONG [KR] ET AL) 2 December 2004 (2004-12-02) the whole document * see claims *	1-20
Y	WO 2004/015801 A1 (HOKU SCIENT INC [US]; TAFT KARI MILTON III [US]; KURANO MATTHEW ROBERT) 19 February 2004 (2004-02-19) the whole document * see claims *	1-20
Y	LI X ET AL: "Evaluation of composite membranes for direct methanol fuel cells", JOURNAL OF POWER SOURCES, ELSEVIER SA, CH, vol. 154, no. 1, 9 March 2006 (2006-03-09), pages 115-123, XP025083760, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2005.03.222 [retrieved on 2006-03-09] the whole document * see p. 117/8, par. 2.3, Composites of ion-conducting polymers ..."	1-20
Y	US 2008/182154 A1 (KIM TAE KYOUNG [KR] ET AL) 31 July 2008 (2008-07-31) the whole document * see [0030] - [0045]; claims *	1-20
Y	JP 2003 282095 A (RIKOGAKU SHINKOKAI) 3 October 2003 (2003-10-03) abstract	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/051531

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			JP 4782102	B2	28-09-2011
			JP 2008184608	A	14-08-2008
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			US 2008182154	A1	31-07-2008

JP 2003282095	A	03-10-2003	NONE		
