

(19)



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11)

N° de publication :

LU501351

(12)

BREVET D'INVENTION**B1**

(21)

N° de dépôt: LU501351

(51)

Int. Cl.:

H01M 4/90, H01M 4/88

(22)

Date de dépôt: 26/10/2020

(30)

Priorité:

(72)

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Date de mise à disposition du public: 10/05/2022

(74)

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Date de délivrance: 10/05/2022

(73)

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HOMOGENEOUS CATALYST AND CATALYST LAYER FOR ANION EXCHANGE MEMBRANE FUEL CELL .

(57)

The present application discloses a homogeneous catalyst and a catalytic layer for an anion exchange membrane fuel cell. The homogeneous catalyst is an ionic polymer with side chains containing a molecular catalyst and quaternary ammonium salt groups, which is prepared by introducing the molecular catalyst of fuel cell cathode or anode into side chains of a polymer with side chains containing bromoalkyl group and performing quaternization on the bromoalkyl group. The homogeneous catalyst is composed of a main chain of hydrophobic polyaromatic hydrocarbons and side chains of hydrophilic quaternary ammonium salts, and can form microphase separation. The molecular catalyst is distributed in hydrophilic ion channels formed by the side chains, resulting in microreactors similar to a homogeneous solution system, and the microreactors are connected through the hydrophilic ion channels. The power density of the fuel cell based on the novel homogeneous catalyst is increased by three times compared with that of a conventional fuel cell with a heterogeneous catalyst, and its stability is significantly improved.

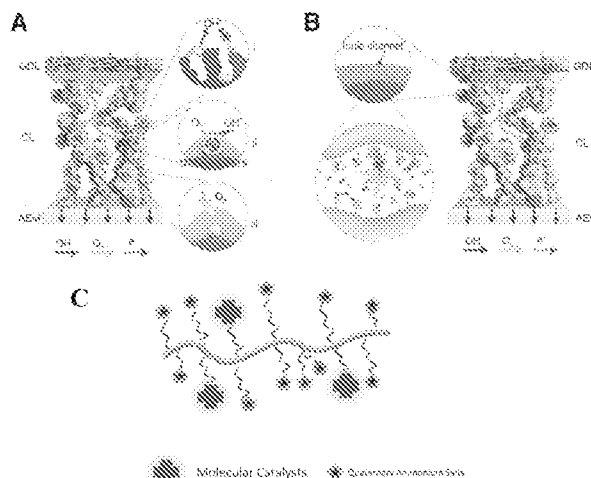


Figure 1

HOMOGENEOUS CATALYST AND CATALYST LAYER FOR ANION EXCHANGE MEMBRANE FUEL CELL

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TECHNICAL FIELD

[0001] The present application belongs to the field of fuel cells, and relates to a homogeneous catalyst, and a catalytic layer for an anion exchange membrane fuel cell.

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BACKGROUND

[0002] As a clean, efficient, safe and green energy conversion device, fuel cells are expected to become the most prominent new technology in new energy applications. Among them, alkaline anion exchange membrane fuel cells have the advantages of high specific power, high power generation efficiency, and environmental friendliness, and at the same time avoid the disadvantages of high cost of precious metal catalysts and high methanol permeability of proton exchange membrane fuel cells, and thus become a high-profile new energy technology. As the core of a fuel cell, the membrane electrode assembly consists of a gas diffusion layer, a catalytic layer and an ion exchange membrane.

[0003] The catalytic layer of fuel cells comprises nanocatalysts such as Pt/C to complete catalytic reactions, as well as ionomers a structure similar to that of the ion-exchange membrane. Ionomers act as both a binder and an ionic conductor, thereby constituting a spatial site where ion conductive material, electronic conductive material, and reactants are together confined to the catalytic site, thus allowing the catalytic reactions to occur. Under ideal conditions, Pt surface would be evenly covered by a thin film of ionomers, but the reality is that during the formation of the catalytic layer, irrespective of the stirring of the ink, a considerable portion of Pt particles will not be covered by the ionomers. As a result, the portion comprises no ionic conduction channels, resulting in low catalyst utilization. On the other hand, agglomeration or excessive coverage of ionomers may hinder gas diffusion, thereby affecting the catalytic efficiency. In addition, even for catalyst nanoparticles that can be uniformly covered by ionomers, since electrocatalysis is a surface interface reaction, the inner atoms of the nanoparticles cannot be effectively used. For example, for 3.9 nm spherical nano-Pt particles, the proportion of the outermost atoms that can play a catalytic role is only 26%. Therefore, it can be seen that the current heterogeneous catalysis-based catalytic

layer structure suffers from several deep-rooted drawbacks: (i) limitations of three-phase interfaces, for example, Pt nanoparticle supports that are not covered by ionomers or located in tiny pores may not complete the catalytic reaction, (ii) the agglomeration of the ionomers, which leads to resistance to oxygen mass transfer, and (iii) insufficient use of the atoms in the core region of the nanoparticles.

[0004] These issues prompted us to consider whether the structure of the catalytic layer can be changed to introduce the concept of homogeneous molecular catalysis. In homogeneous catalysis, the catalyst and the reactant exist in the same media in molecular state, so the homogeneous catalyst has a higher utilization rate, avoids the mass transfer problem of the heterogeneous catalyst, and has better catalytic selectivity. However, despite the studies on the immobilization of molecular catalysts on the surface of carbon supports or gas diffusion electrodes, there are few reports on the achieving homogeneous catalytic systems in fuel cells. The difficulty of achieving homogeneous catalysis in the catalytic layer of fuel cells lies in how to embed the molecular catalysts evenly and stably into the medium where oxygen, ions and electrons can reach. In the ionomer film of the catalyst layer, phase separation occurs through hydrophilic-hydrophobic interactions, in which the hydrophilic part of the ionic group constitutes ionic nanochannels, which can be considered as homogeneous systems from a local perspective. Therefore, in order to apply the concept of homogeneous catalysis to the catalyst layer of fuel cells, the molecular catalysts must be placed in the ion channels where the electroactive species are located.

[0005] The present application discloses an ionomer comprising a molecular catalyst in side chains. The molecular catalyst is distributed on the side chains, so the obtained catalyst complex has a high density of active sites, which are randomly dispersed in an ionic conductive media. This strategy establishes a novel stable homogeneous catalytic system like interconnected nanoreactors, and most importantly, each catalyst molecule anchored in the ion channels can serve as an active center at the “three-phase interface”, and can theoretically be 100% utilized.

SUMMARY

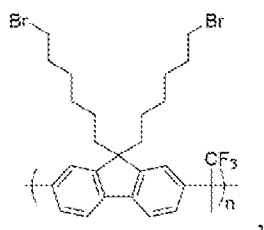
[0006] Regarding the deficiencies of the prior art, the present application provides a homogeneous catalyst and a catalytic layer for an anion exchange membrane fuel cell. By designing and synthesizing an ionic polymer with side chains containing a molecular catalyst and quaternary ammonium salts, and applying it as a homogeneous catalyst in the catalytic layer of the fuel cell, the utilization rate of the catalyst is greatly increased, the mass transfer of the catalytic layer is

improved, and the performance of the fuel cell is improved.

[0007] Provided herein is a homogeneous catalyst, which is an ionic polymer with side chains containing a molecular catalyst and quaternary ammonium salt groups, wherein the ionic polymer is prepared by introducing the molecular catalyst of fuel cell cathode or anode into side chains of a polymer with side chains containing bromoalkyl group and performing quaternization on the

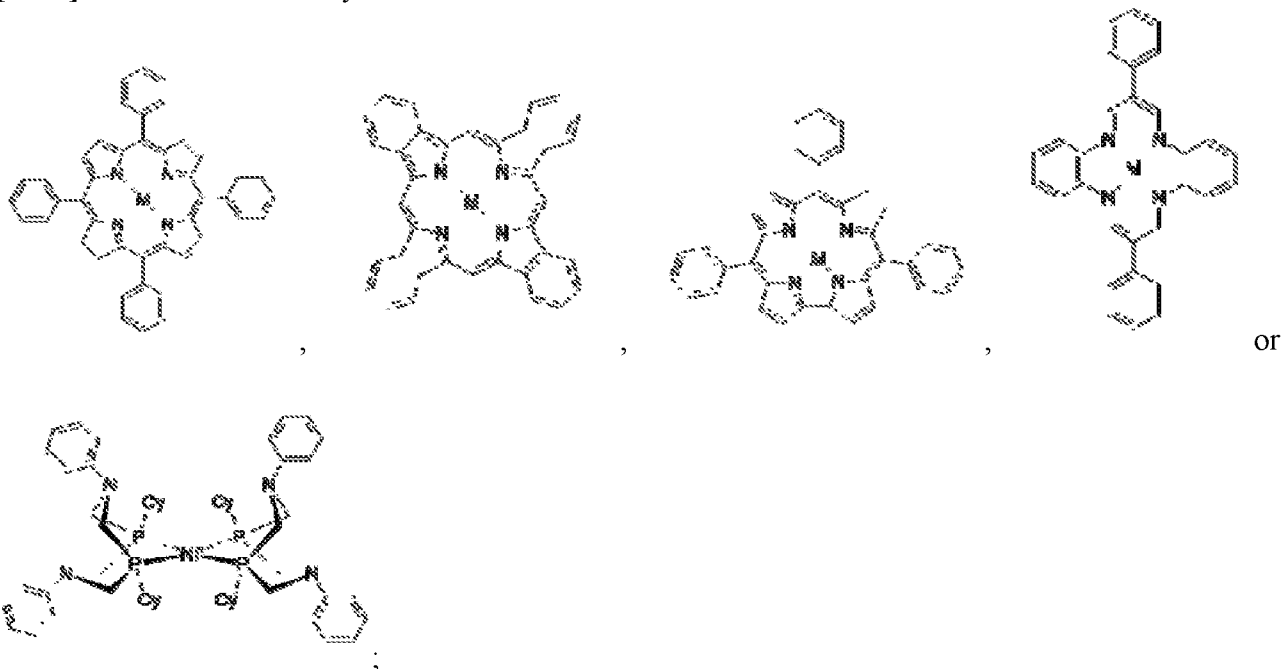
wherein the molecular catalyst is a metal complex catalyst containing porphyrins, phthalocyanines or corroles;

the polymer with side chains containing bromoalkyl group is bromoalkyl polyfluorene having a structure as below:



wherein n is the degree of polymerization.

[0008] The molecular catalyst is selected from:



wherein M is Fe, Co, Cu, Ni or Pt.

[0009] The method for introducing the molecular catalyst into the side chains of the polymer comprises: subjecting the molecular catalyst to a substitution reaction, and then reacting the substituted molecular catalyst with the bromine in the bromoalkyl side chain on the polymer to form

a covalent bond, thereby attaching the molecular catalyst to the side chains of the polymer. For instance, the molecular catalyst can be subjected to a substitution reaction to form a phenolic hydroxyl group on the molecular catalyst, and then the phenolic hydroxyl group of the molecular catalyst is reacted with the bromine in the bromoalkyl group on the polymer to form an ether bond, thereby attaching the molecular catalyst to the side chains of the polymer.

[0010] Further, the molar ratio of the molecular catalyst to the bromoalkyl group on the polymer is 1:10-1:2.

[0011] Provided herein is a catalytic layer for an anion exchange membrane fuel cell based on a homogeneous catalyst, which is obtained by formulating the above-mentioned homogeneous catalyst, conductive carbon black, and N,N-dimethyl formamide into a catalyst slurry, coating the slurry on a gas diffusion layer material, and drying the coating, wherein phase separation occurs through hydrophilic-hydrophobic interactions (between the hydrophilic side chains and the hydrophobic main chain) in the catalytic layer, while the molecular catalyst is distributed in hydrophilic ion channels formed by the side chains, resulting in microreactors similar to a homogeneous solution system, wherein the microreactors are connected through the hydrophilic ion channels.

[0012] The present application has the following beneficial effects:

In the present application, a homogeneous catalytic system in the catalyst layer for an anion exchange membrane fuel cell is obtained by immobilizing a molecular catalyst in side chains of ionomers and distributing it in ion channels. In the constructed homogeneous catalyst layer, the molecular catalyst is distributed along the ion channels, which greatly increases catalyst utilization and improves mass transfer. The molecular catalyst is covalently bonded to the ionomers, and the catalyst exhibits excellent electrochemical stability. The homogeneous system also improves atomic efficiency and exhibits higher peak power density in single cell tests of the fuel cells, indicating improved mass transfer in the homogeneous catalyst layer. This design strategy of a catalytic layer based on a homogeneous catalyst can also be extended to other electrochemical energy conversion devices to fulfill the practical application of non-noble metal materials by simply improving mass transfer and catalytic site utilization.

[0013] BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a comparison of a conventional catalytic layer based on a heterogeneous catalyst (A) and the catalytic layer based on the homogeneous catalyst provided by the present

application (B), and a schematic illustration of the structure of the homogeneous catalyst in the present application (C).

Figure 2 is the synthetic route of homogeneous catalyst PF-TMPPCo.

Figure 3 is the synthetic route of homogeneous catalyst PF-PcFe.

Figure 4 shows the basic characterization of the homogeneous catalyst PF-TMPPCo, demonstrating the successful synthesis of the material.

Figure 5 shows the micromorphology of the homogeneous catalyst after carbon loading.

Figure 6 shows the micromorphology and element distribution of the homogeneous catalyst. The molecular catalysts are uniformly distributed in ion channels constructed by the quaternary ammonium salt groups in the side chains.

Figure 7 shows a comparison of the oxygen reduction activity of the homogeneous catalyst and other heterogeneous catalysts.

Figure 8 shows the turnover frequencies (TOF) of metal centers in different catalysts. Among them, the homogeneous catalyst exhibited the highest TOF.

Figure 9 shows the stability of the homogeneous catalyst PF-TMPPCo.

Figure 10 shows the fuel cell polarization curves of homogeneous catalyst PF-TMPPCo, heterogeneous blend catalyst PFI-TMPPCo and PFBr-TMPPCo without quaternary ammonium salts.

Figure 11 is the hydrogen oxidation curves of the molecular catalyst TMPPPt at different rotation speeds.

DETAILED DESCRIPTION

[0014] Materials and instruments

Sodium hydroxide, dimethylformamide (DMF), anhydrous ether, trimethylamine, potassium carbonate, methanol, cobalt acetate, and ferric chloride were purchased from Sinopharm Chemical Reagent Co. Ltd. Bromhexyl fluorene and hydroxyphenyl-trimethoxyphenylporphyrin cobalt were synthesized. Bromhexyl polyfluorene was prepared by the polymerization of bromohexyl fluorene and trifluoroacetone under the catalysis of trifluoromethanesulfonic acid.

[0015] Figure 1 shows a comparison of a conventional Pt-based catalytic layer and the carbon-doped PF-TMPPCo catalytic layer of the present application. In this figure, A shows the conventional catalytic layer and sites where the reaction cannot be completed, including i, Pt nanoparticles without covering of the ionomers; ii, unused central atoms of the Pt nanoparticles; and

iii, over-covered ionomers, which affect the delivery of reactive gases; and B is the schematic illustration of the novel homogeneous catalytic layer, showing that the molecular catalysts are distributed in ion channels composed of the ionomers, thereby forming interconnected microreactors.

5 [0016] Example 1

Preparation of bromhexyl polyfluorene-tetramethoxyphenylporphyrin cobalt ionomer (PF-TMPPCo) homogeneous catalyst

PF-TMPPCo was prepared by one-pot modification of bromhexyl polyfluorene as below: a solution of hydroxyphenyl-trimethoxyphenylporphyrin cobalt (TMPPCo-OH, 588 mg), K_2CO_3 (150 mg), and bromhexyl polyfluorene (PF, 1.44 g) in DMF (100 mL) was stirred at 80°C for 24 h under an N_2 atmosphere. After the TMPPCo was attached to the PF side chain, 2 mL of trimethylamine (30 wt% in ethanol) was added into the reaction and the reaction mixture was reacted at 50°C for 24 h in a sealed system. Subsequently, the reaction solution was poured into water to precipitate any solid material. The suspension was sonicated, washed and centrifuged three times with 0.1 M hydrochloric acid and deionized water to remove any excess reactants. The obtained catalyst was vacuum-dried at 60°C for 24 h and directly used as an electrochemical catalyst after mixing with a carbon material.

Figure 2 is the representative synthetic route of homogeneous PF-TMPPCo catalyst. Under the catalysis of a superacid, bromoalkyl fluorene reacted with trifluoroacetone to yield bromoalkyl polyfluorene, and then the catalytic center was bonded to the PF side chain through the reaction of the bromoalkyl group in the side chain and the hydroxyl-substituted tetramethoxyphenylporphyrin cobalt, and finally the remaining bromoalkyl group was reacted with trimethylamine to obtain a quaternized polymer catalyst.

[0017] Example 2

25 **Preparation of bromhexyl polyfluorene-ferrous phthalocyanine ionomer (PF-PcFe) homogeneous catalyst**

PF-PcFe was prepared by two-step modification of bromhexyl polyfluorene as below: a solution of tetrahydroxy ferrous phthalocyanine (500 mg), K_2CO_3 (150 mg), and bromhexyl polyfluorene (PF, 1.44 g) in DMF (100 mL) was stirred at 80°C for 24 h under an N_2 atmosphere, and then precipitated in methanol to yield a dark green polymer solid. After the PcFe was attached to the PF side chain, 2 mL of trimethylamine (30 wt% in ethanol) was added into the reaction and the reaction mixture was reacted at 50°C for 24 h in a sealed system. Subsequently, the reaction

solution was poured into water to precipitate any solid material. The suspension was sonicated, washed and centrifuged three times with 0.1 M hydrochloric acid and deionized water to remove any excess reactants. The obtained catalyst was vacuum-dried at 60°C for 24 h and directly used as an electrochemical catalyst after mixing with a carbon material.

Figure 3 is the representative synthetic route of homogeneous PF- PcFe catalyst.

[0018] Example 3

Electrochemical characterization of the catalysts

Electrochemical measurements were conducted using an Autolab PGSTAT302N potential stat with reference to a freshly made reversible hydrogen electrode (RHE) and a platinum wire as the counter electrode in a solution of 0.1 M KOH. The catalyst ink was prepared by mixing the catalyst powder (1 mg), PF ionomer (1 mg), and ECP carbon (10 mg) in 4 mL DMF (the PF ionomer is not necessary when the catalyst powder is the homogeneous catalyst prepared in the present application). The resulting suspension was sonicated for 1 h and then cast onto the surface of a glassy carbon (GC) electrode (OD = 5.61 mm, PINE) using a 10 μ L micropipette. The electrode was dried in an isopropanol-saturated atmosphere. Each suspension was freshly prepared before conducting the experiments. The electrolyte was saturated with Ar or O₂ by bubbling Ar or O₂ prior to the start of each measurement for 30 min. The flow of Ar or O₂ was continuously bubbled above the electrolyte during measurement to ensure the saturation of Ar or O₂. CV and RDE measurements were all carried out in Ar-saturated or O₂-saturated 0.1 M KOH solution at a scan rate of mV s⁻¹.

[0019] Example 4

Preparation and single cell testing of the catalytic layer for anion exchange membrane fuel cells

To prepare the electrocatalyst slurry, the catalyst ink was prepared by weighing and mixing the catalyst powder (10 mg), PF ionomer (10 mg), and ECP carbon (100 mg) in 40 mL DMF (the PF ionomer is not necessary when the catalyst powder is the homogeneous catalyst prepared in the present application). Then, the mixture was transferred to a glass vial that was submerged in a water sonication bath and left for 30 min to yield a homogenized slurry mixture. Once the sonication was complete, the mixture was sprayed onto Toray carbon paper (25 cm², non-teflonated, TGP-H-60) using a hand-held spray gun linked to a nitrogen gas line for pressure to obtain a catalyst metal loading of 0.80 mg $\pm$ 0.08 mg/ cm². The PtRu/C anodes were prepared in a similar way, reaching the metal loading as above. All the spray-coated catalyst and the HDPE-25 μ m membrane were

soaked in a 1 M KOH solution for 1 hour, and then the solution was exchanged with fresh KOH solution, so as to activate the quaternary ammonium salt groups. Then they were assembled in a cell as a membrane electrode assembly (MEA). The prepared MEAs were correspondingly sandwiched between two gaskets (thickness = 0.15 mm) and sealed into the test unit at a constant torque of 5.5 Nm, using retaining bolts and a torque driver. A fuel Cells[®] software version 4 (Scribner Associates) was used to record the galvanostatic polarization curves of the fuel cell.

[0020] Figure 4 is the characterization of the PF-TMPPCo catalyst structure, in which:

A, FT-IR spectra of PF, TMPPCo and PF-TMPPCo;

B, UV-vis spectra of PF, TMPPCo and PF-TMPPCo;

C, High-resolution XPS Co 2p spectra of TMPPCo and PF-TMPPCo; and

D, Co K-edge XANES spectra of TMPPCo and PF-TMPPCo.

As can be seen, both the FT-IR spectra and UV-vis spectra of PF-TMPPCo have the signals of PF and TMPPCo, indicating that TMPPCo was successfully bonded to PF. Meanwhile, the XPS spectra and XANES spectra of PF-TMPPCo are similar to those of TMPPCo, indicating that the Co-N₄ active site was preserved during bonding.

[0021] Figure 5 shows the microphase separation structure of the catalyst, in which: A, SEM image of PF-TMPPCo; B, TEM image of PF-TMPPCo; C, elemental image of PF-TMPPCo; and D, elemental image of PFI-TMPPCo. Similar to conventional PtC catalysts, PF Ionomer is coated on the outer of carbon nanospheres to form a porous catalytic layer structure. At the same time, the Co element distribution of PF-TMPPCo is more uniform than that of PFI-TMPPCo.

[0022] Figure 6 shows the micromorphology of the catalyst, in which: A, atomic-resolution highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of PF-TMPPCo (single Co atoms showing bright contrast); B, energy-dispersive X-ray spectroscopy images of PF-TMPPCo; C, net-scanning intensity profile from the area indicated with a green rectangle in Figure 3b, the light blue rectangle corresponds to the ionic channel region; D, simulated configurations of PF-TMPPCo and E, PFI-TMPPCo (mixture of PF ionomer and TMPPCo): Co (yellow), O (red), N (purple), F (green) and C (grey), in which left panel is a complete graph, right panel comprises Co atoms only for clarity and the red cycle highlights the aggregation of porphyrin rings in PFI-TMPPCo.

[0023] Figure 7 shows the ORR polarization curves of different catalysts at 900 rpm. PF-TMPPCo exhibited the highest half-wave potential. Figure 8 shows the turnover frequencies (TOF) of metal centers in different catalysts. Among them, the homogeneous catalyst exhibited the highest TOF.

Figure 9 shows the stability of the homogeneous catalyst PF-TMPPCo. After testing for 20000 cycles, PF-TMPPCo had only a half-wave attenuation of 15 mV, proving its excellent stability. Figure 10 shows the fuel cell polarization curves of homogeneous catalyst PF-TMPPCo, heterogeneous blend catalyst PFI-TMPPCo and PFBr-TMPPCo without quaternary ammonium salts. The homogeneous catalyst exhibited superiority in the fuel cells. Figure 11 is the hydrogen oxidation curves of the molecular catalyst TMPPPt at different rotation speeds. It can be seen that the homogeneous catalyst prepared by the present application is also suitable for anode.

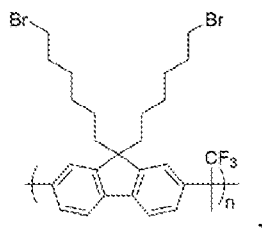
CLAIMS

5 WHAT IS CLAIMED IS:

1. A homogeneous catalyst, which is an ionic polymer with side chains containing a molecular catalyst and quaternary ammonium salt groups, wherein the ionic polymer is prepared by introducing the molecular catalyst of fuel cell cathode or anode into side chains of a polymer with side chains containing bromoalkyl group and performing quaternization on the bromoalkyl group;

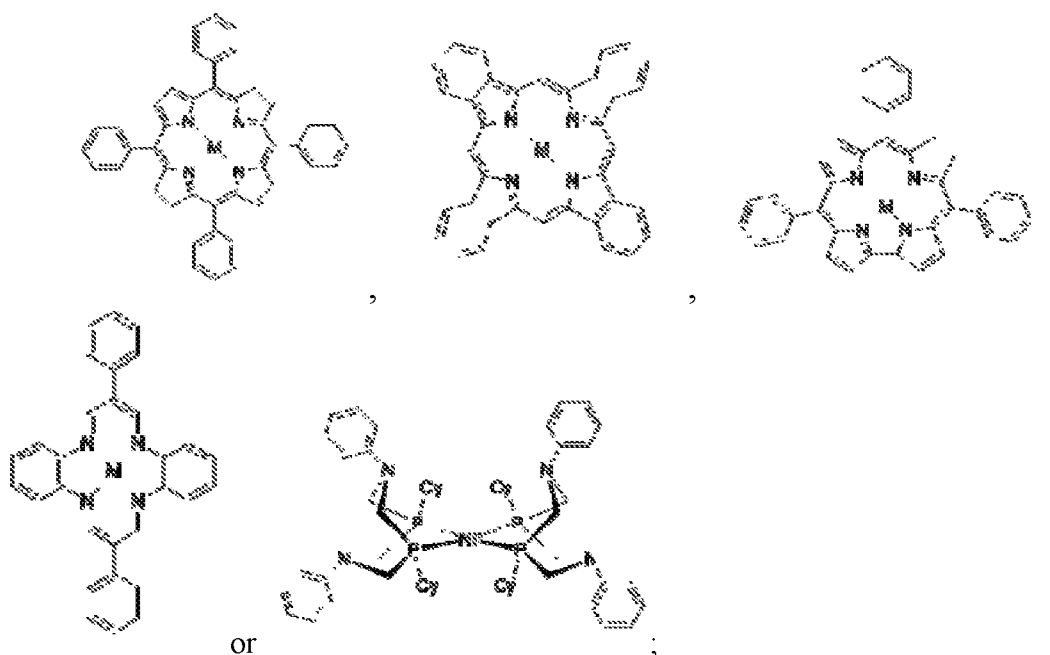
10 wherein the molecular catalyst is a metal complex catalyst containing porphyrins, phthalocyanines or corroles;

the polymer with side chains containing bromoalkyl group is bromoalkyl polyfluorene having a structure as below:



15 wherein n is the degree of polymerization.

2. The homogeneous catalyst according to claim 1, wherein the molecular catalyst is selected from:



wherein M is Fe, Co, Cu, Ni or Pt.

3. The homogeneous catalyst according to claim 1, wherein the method for introducing the molecular catalyst into the side chains of the polymer comprises: subjecting the molecular catalyst to a substitution reaction, and then reacting the substituted molecular catalyst with the bromine in the bromoalkyl side chain on the polymer to form a covalent bond, thereby attaching the molecular catalyst to the side chains of the polymer.

4. The homogeneous catalyst according to claim 1, wherein the molar ratio of the molecular catalyst to the bromoalkyl group on the polymer is 1:10-1:2.

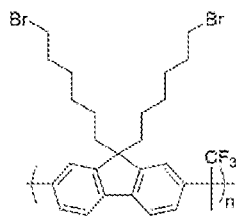
5. A catalytic layer for an anion exchange membrane fuel cell based on a homogeneous catalyst, which is obtained by formulating the homogeneous catalyst of any one of claims 1-4, conductive carbon black, and N,N-dimethyl formamide into a slurry, coating the catalyst slurry on a gas diffusion layer material, and drying the coating, wherein phase separation occurs through hydrophilic-hydrophobic interactions in the catalytic layer, while the molecular catalyst is distributed in hydrophilic ion channels formed by the side chains, resulting in microreactors similar to a homogeneous solution system, wherein the microreactors are connected through the hydrophilic ion channels.

Ansprüche

1. Ein homogener Katalysator, dadurch gekennzeichnet, dass der eine Art ionisches Seitenkettenpolymer ist, das einen molekularen Katalysator und eine quartäre Ammoniumsalzgruppe enthält, das durch Einführen des molekularen Katalysators der Brennstoffzellenkathode oder -anode in die eine Bromalkylgruppe enthaltenen Seitenkette und dann durch Quaternisierung der Bromalkylgruppe erhalten wird;

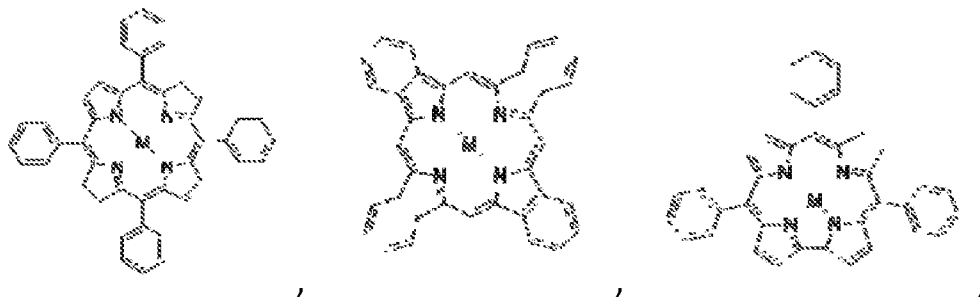
wobei der molekulare Katalysator ein Metallkomplexbkatalysator ist, der Porphyrin, Phthalocyanin oder Carrol enthält;

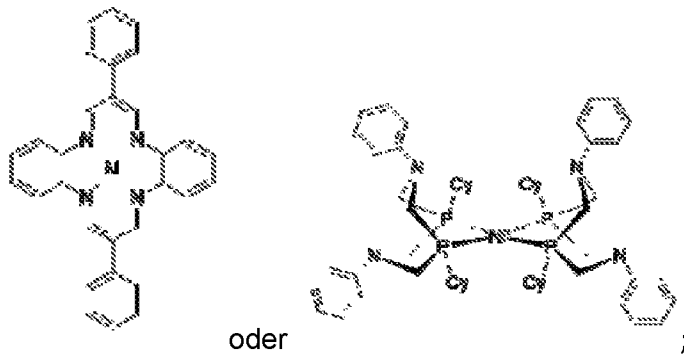
das Polymer, das Bromalkyl in der Seitenkette enthält, Polybromalkylfluoren ist, und die Struktur wie folgt ist:



wobei n der Aggregationsgrad ist.

2. Homogener Katalysator nach Anspruch 1, dadurch gekennzeichnet, dass der molekulare Katalysator aus folgen ausgewählt ist:





wobei M Fe, Co, Cu, Ni oder Pt ist.

3. Homogener Katalysator nach Anspruch 1, dadurch gekennzeichnet, dass das Verfahren zum Einführen des molekularen Katalysators in die Seitenkette des Polymers ist: Unterwerfen des molekularen Katalysators einer Substitutionsreaktion und dann Umsetzen des substituierten molekularen Katalysators mit dem Brom in der Bromalkylseitenkette auf dem Polymer, um eine kovalente Bindung zu bilden, wodurch der molekulare Katalysator an die Seitenketten des Polymers gebunden wird.

4. Homogener Katalysator nach Anspruch 1, dadurch gekennzeichnet, dass das Molverhältnis des molekularen Katalysators zur Bromalkylgruppe am Polymer 1:10–1:2 beträgt.

5. Katalytische Schicht auf der Basis eines homogenen Katalysators für eine Anionenaustauschmembran-Brennstoffzelle, dadurch gekennzeichnet, dass der homogene Katalysator nach einem der Ansprüche 1-4, leitfähiger Ruß und N,N-Dimethylformamid zu einer Katalysatoraufschlämmung formuliert sind, und die Katalysatoraufschlämmung auf das Gasdiffusionsschichtmaterial aufgetragen und getrocknet ist, um eine Katalysatorschicht zu erhalten, und in der katalytischen Schicht der homogene Katalysator aufgrund der hydrophil-hydrophoben Wechselwirkung phasengetreunt ist, und der molekulare Katalysator in dem durch die Seitenkette gebildeten hydrophilen Ionenkanal verteilt ist, wodurch Mikroreaktoren ähnlich einem homogenen Lösungssystem gebildet wird, wobei diese Mikroreaktoren durch hydrophilen Ionenkanal verbunden sind.

FIGURE

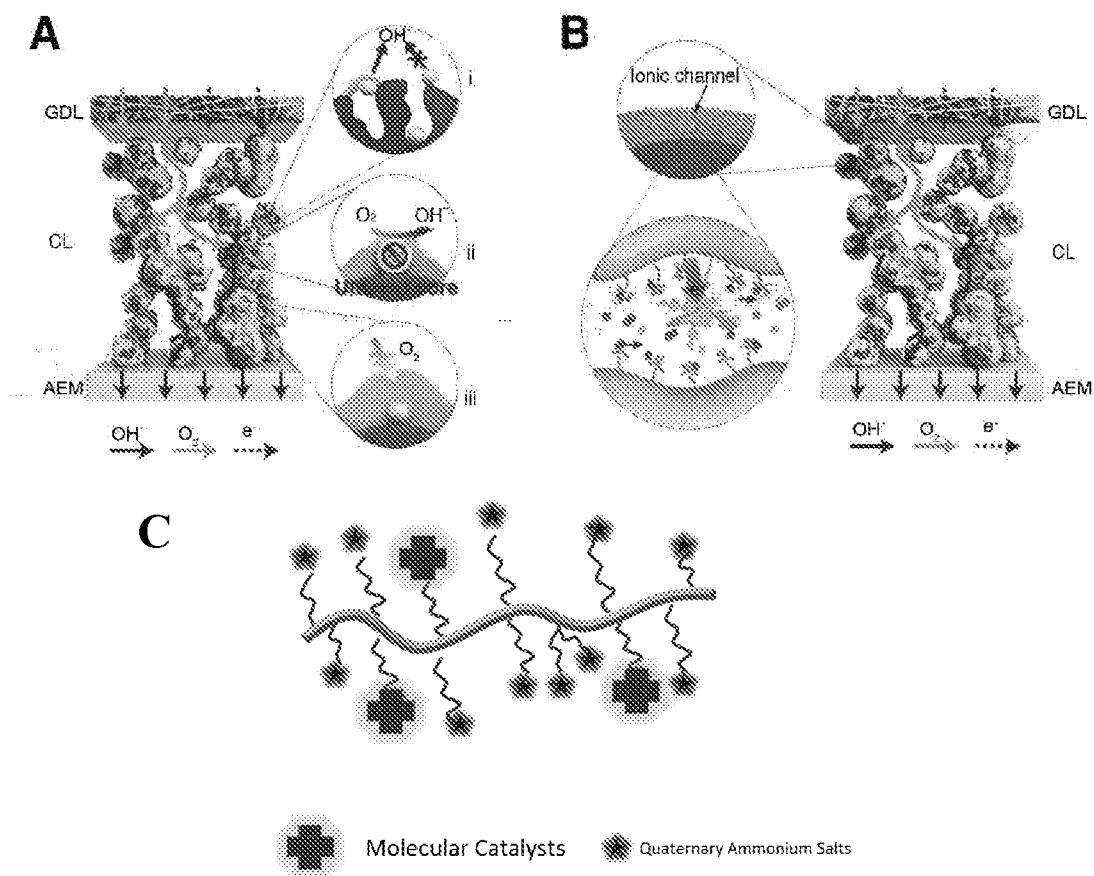


Figure 1

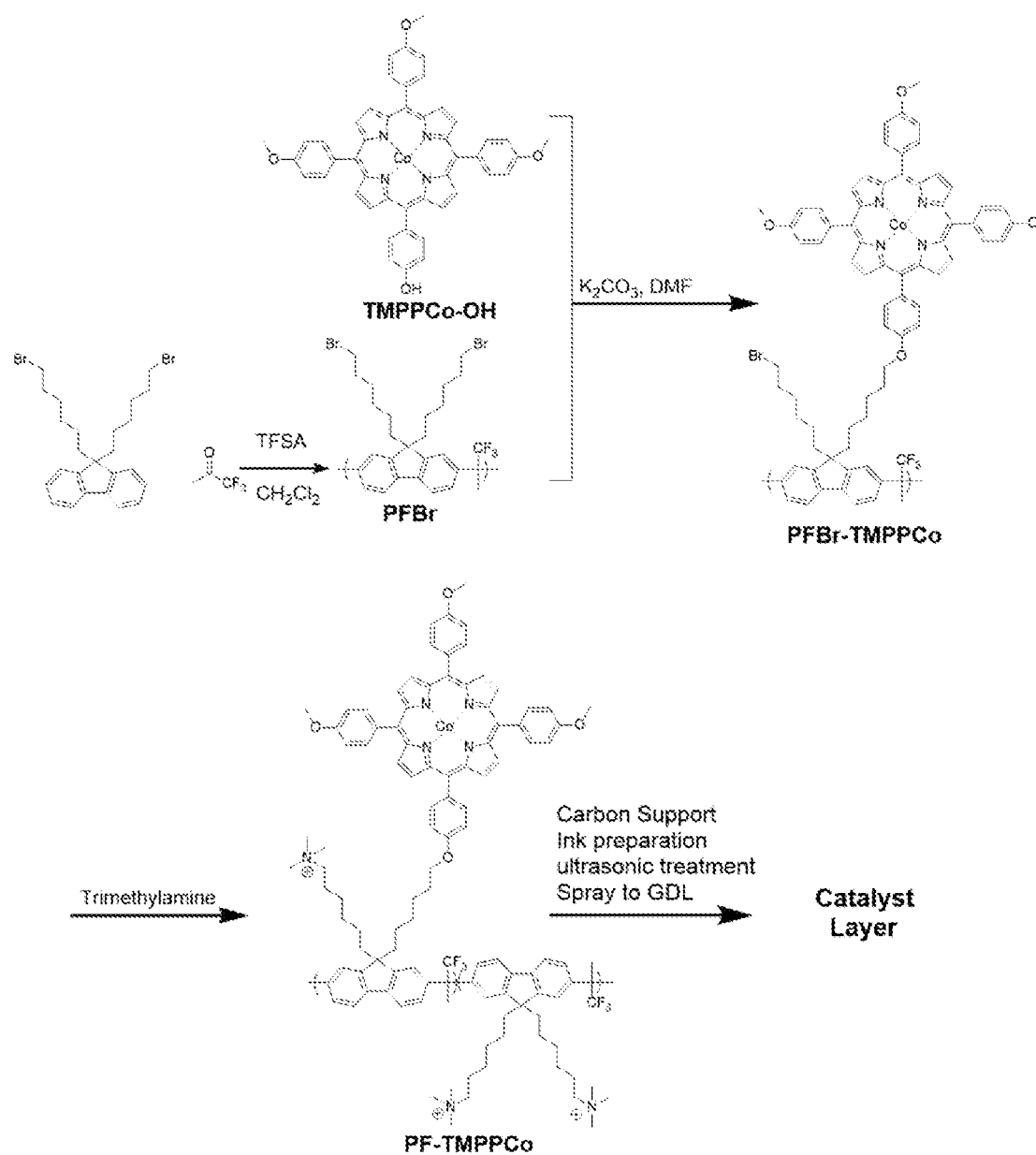


Figure 2

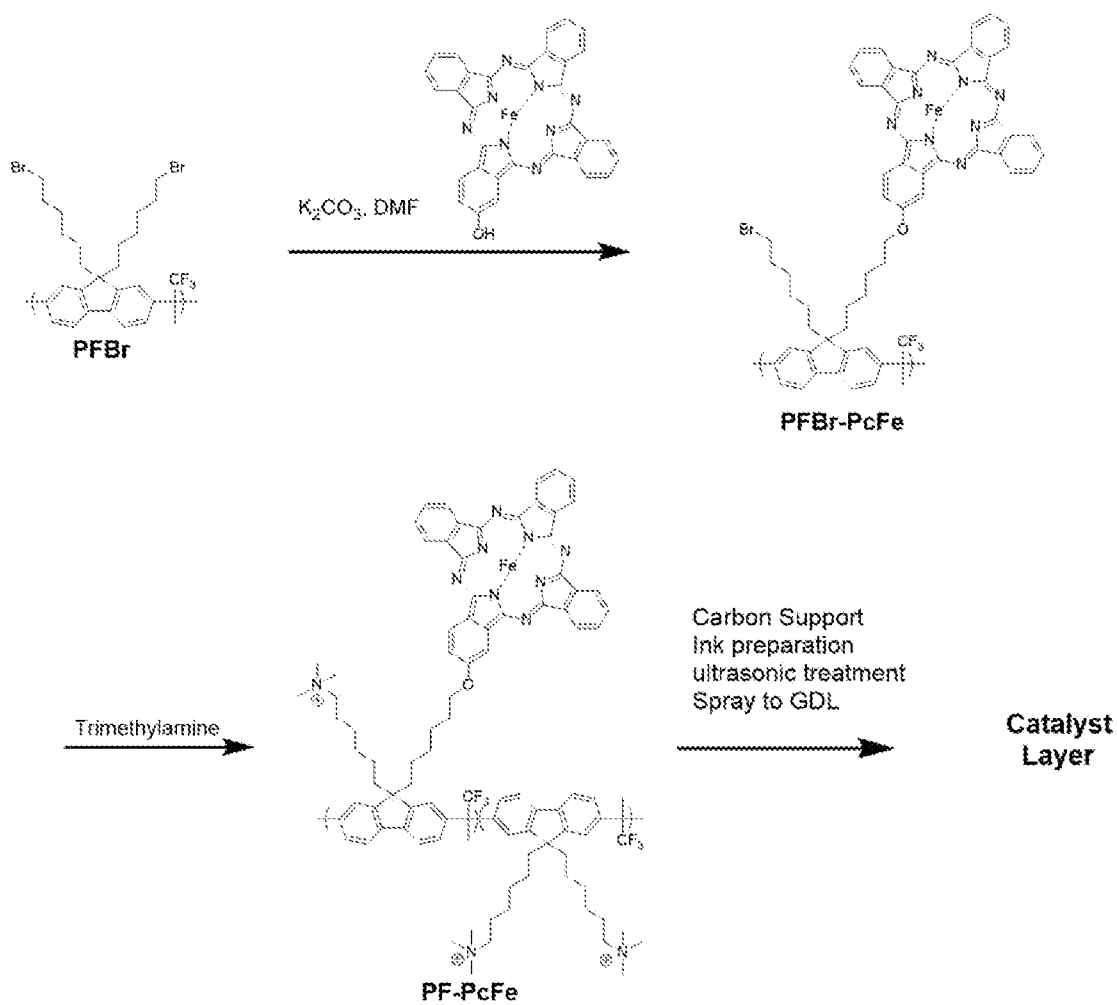


Figure 3

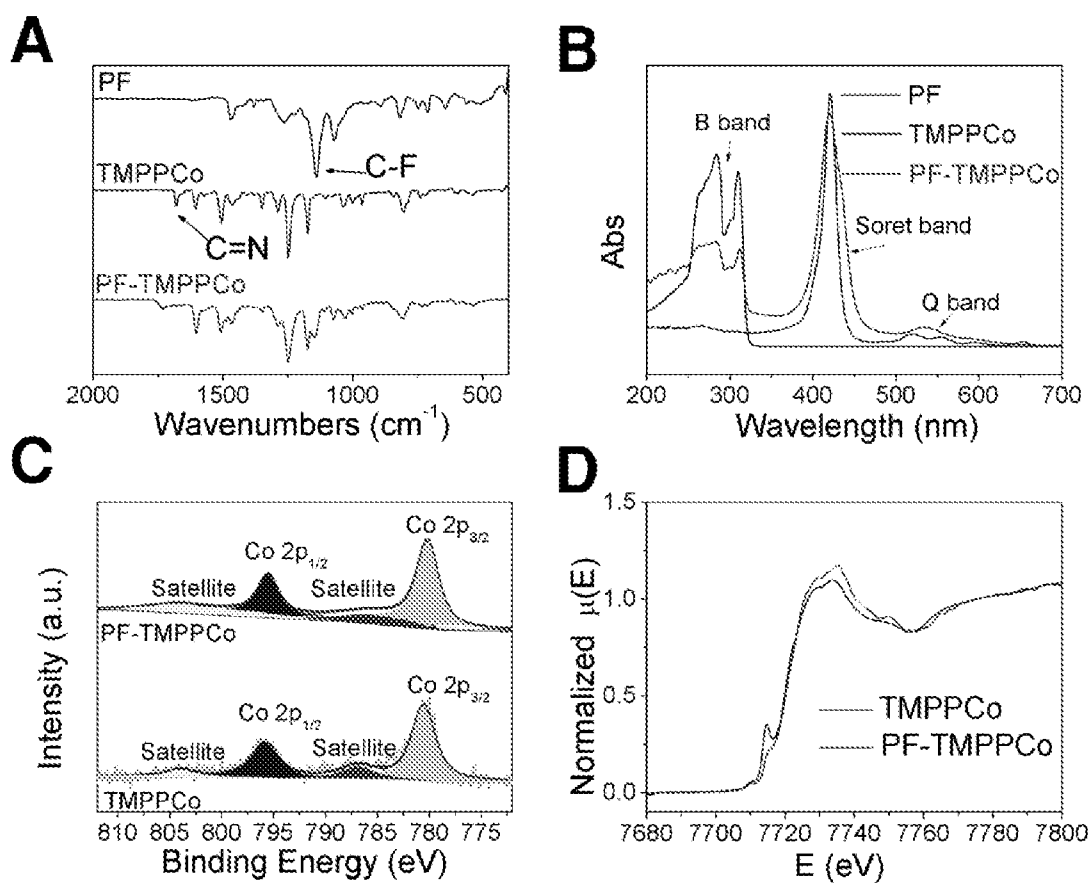


Figure 4

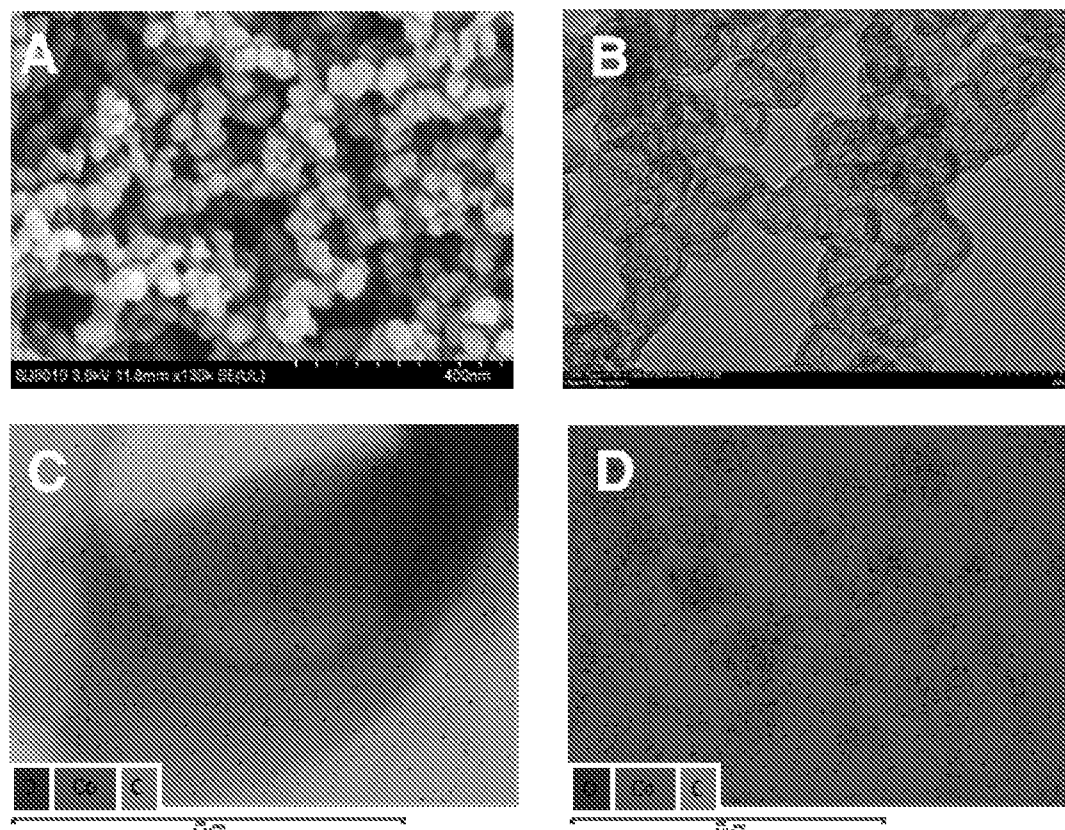


Figure 5

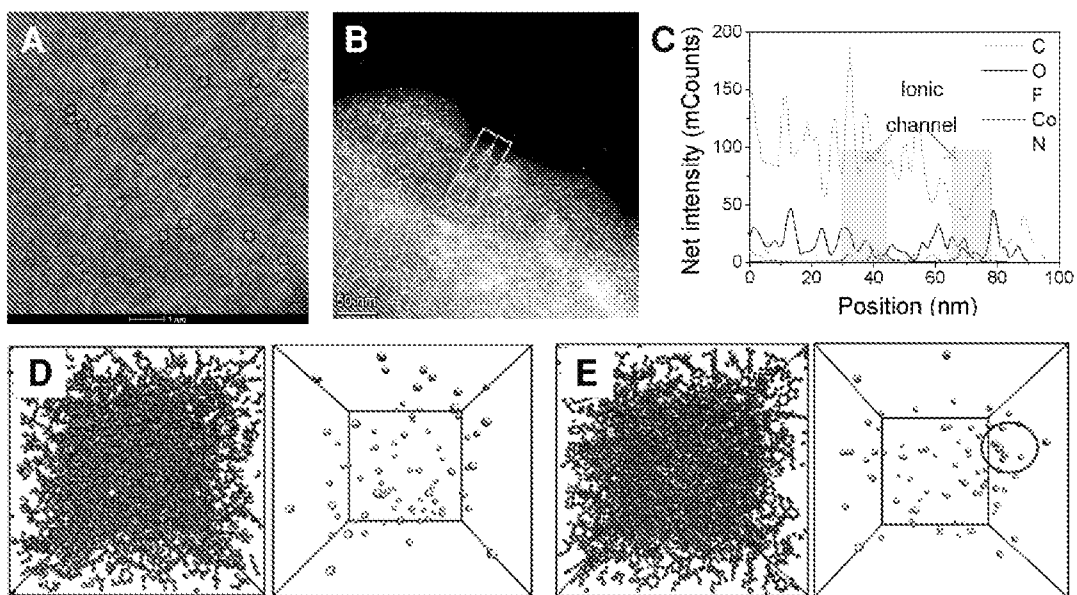


Figure 6

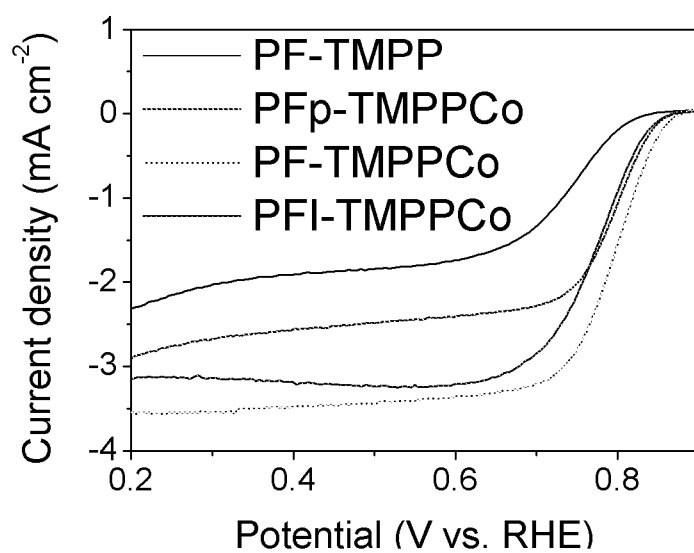


Figure 7

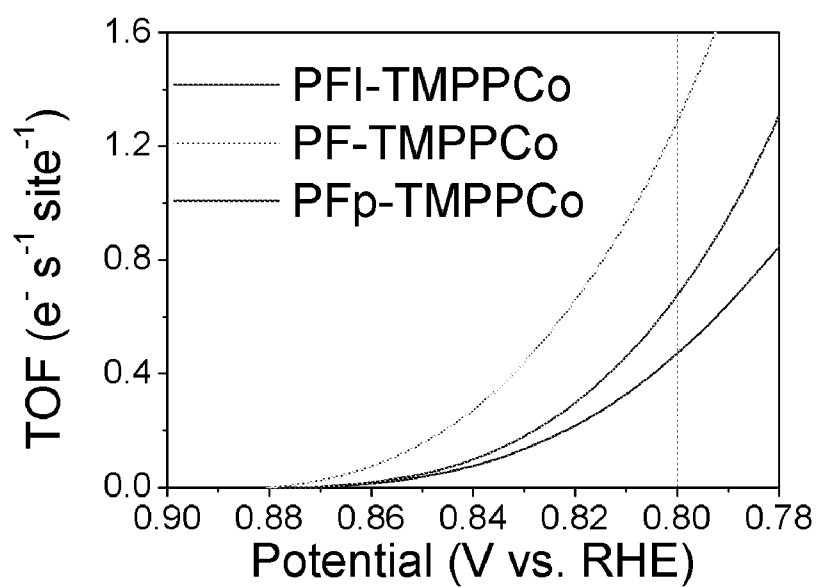


Figure 8

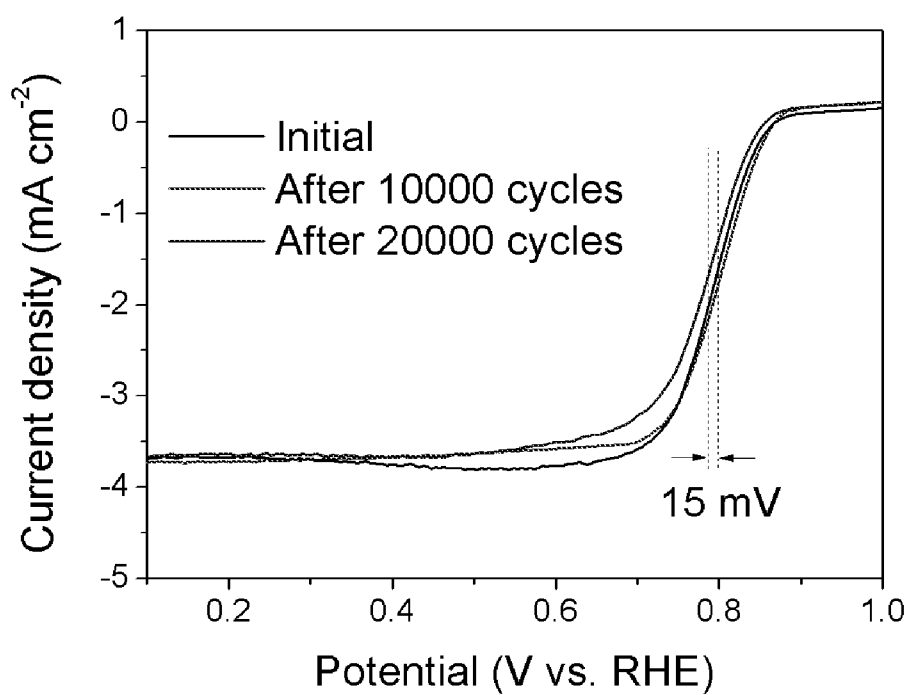


Figure 9

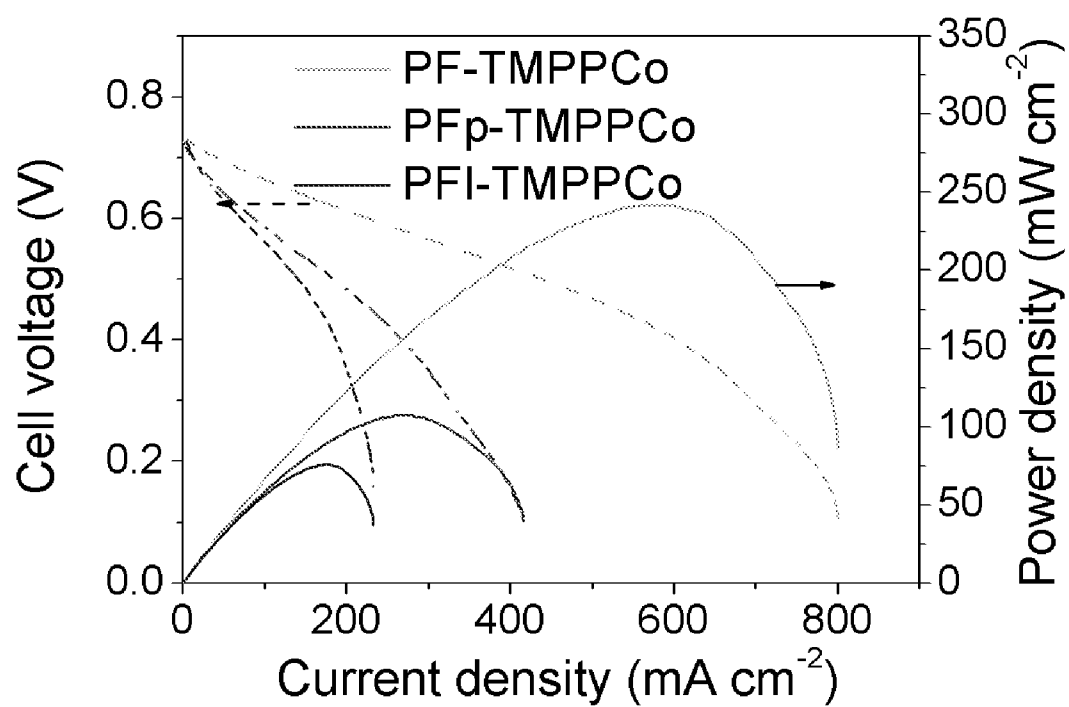


Figure 10

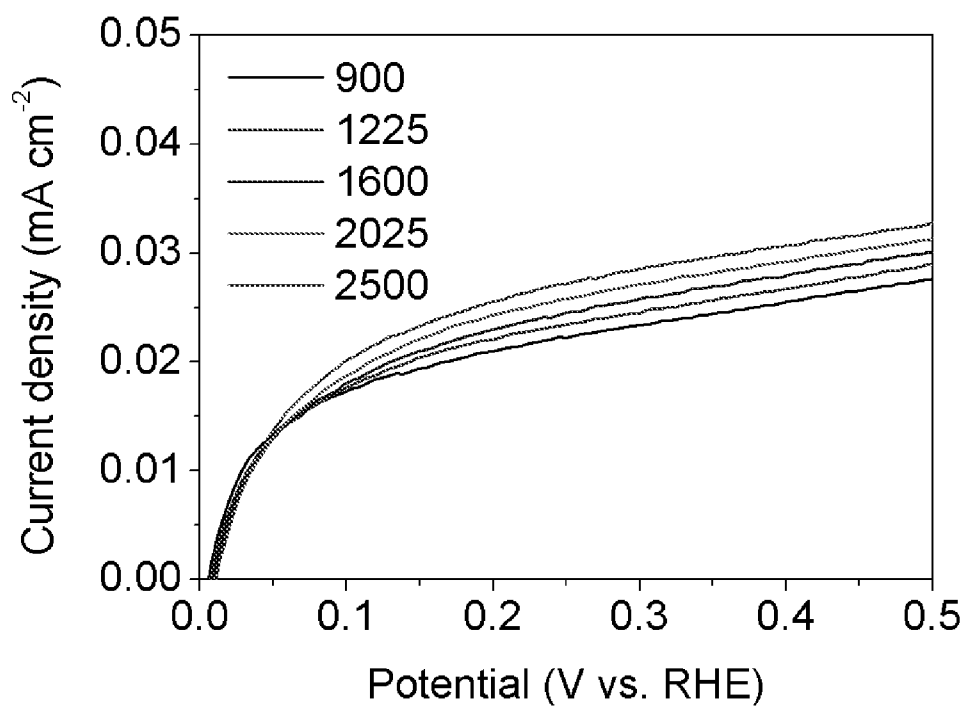


Figure 11