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(54) Title: TITANIUM DIOXIDE DOPED WITH FLUORINE AND PROCESS FOR THE PRODUCTION THEREOF

Figure 1



HR-TEM image

(57) Abstract: A crystalline titanium dioxide containing fluorine atoms within the crystal lattice comprising atoms of titanium and oxygen is described; this titanium dioxide is particularly suitable for the production of solid-state electrolytes, hybrid membranes for fuel cells or electrolyzers. The aforesaid titanium dioxide may be produced using a process comprising the following stages: (a) a titanium ore is reacted with a NH_4HF_2 aqueous solution; (b) the aqueous dispersion thus obtained is filtered with consequent separation of a solid residue and an aqueous solution containing titanium salts; (c) the aqueous solution thus obtained is subjected to hydrolysis, said hydrolysis comprising a first stage at pH 6.5-8.0 and a second stage at pH 9-11; (d) the aqueous dispersion thus obtained is filtered and the solid residue is subjected to pyrohydrolysis at a maximum temperature of approximately 500°C, preferably approximately 450°C.

Titanium dioxide doped with fluorine and process for the production thereof

The invention relates to fluorine-doped titanium dioxide (TiO_2); this titanium dioxide may advantageously be used in the manufacture of inorganic/organic hybrid membranes. The resulting membranes are characterised by better proton conductivity and mechanical properties than those demonstrated by similar systems which do not include doped titanium dioxide. Furthermore the proton conductivity and the performance of some resulting inorganic/organic hybrid membranes in PEMFC fuel cells are less compromised by dehydration than similar systems which do not include doped titanium dioxide. It may also be used in the production of solid-state electrolytes.

State of the art

A fuel cell is a device which converts the chemical energy of the reagents fed to it directly into electrical energy. Fuel cells are well known in the art and are for example described in Cappadonia *et al.*, Ullmann's Encyclopedia of Industrial Chemistry, *Fuel Cells*, 2005, 1-23, Wiley-VCH, which is included here for reference.

Given that a fuel cell is an electrochemical device and not a heat engine, it can easily achieve very high efficiencies, even more than twice those characteristic of conventional combustion engines. There are many different families of fuel cells distinguished by the materials from which they are made and the temperature at which they operate in optimum mode. One of the most intensively studied families is the one including polymer electrolyte fuel cells (Proton Exchange Membrane Fuel Cells, PEMFC). PEMFC operate at low temperature ($T < 130\text{ }^\circ\text{C}$) and comprise a polymer membrane capable of conducting protons (Proton Exchange Membrane, PEM) separating two porous electrodes through which reagents and reaction products can diffuse (Gas Diffusion Layers, GDL). These are covered with a layer of electrocatalysing material used to promote the electrochemical reactions involved in the functioning of the device. PEMFC are silent devices with no moving parts, of simple construction, that are capable of achieving high efficiencies (even over 55%) and are characterised by high energy and power densities. Also, PEMFC do not produce fine powders or pollutants

such as sulphur or nitrogen oxides (SO_x and NO_x) and, if fed with pure hydrogen, the only product of their operation is water. All these characteristics make PEMFC particularly suitable devices for providing power for vehicles or portable electronic devices such as multimedia readers, portable computers and other devices, without causing any harm to the environment.

The core of every PEMFC is the proton conducting membrane, through which protons obtained at the anode following oxidation of the fuel can be transported to the cathode where they are recombined with the products of the reducing reaction of the oxidising agent. The latter generally comprises oxygen present in the air. The most widely used materials in manufacturing proton exchange membranes are perfluorinated copolymers such as Nafion™, Hyflon-Ion, Dow polymer and others. All these materials comprise a main perfluorinated polymer chain, similar to that of Teflon™, from which there extend perfluoroether side chains terminating in an $-\text{SO}_3\text{H}$ group characterised by high acidity. These materials are capable of conducting protons in that, as soon as water is present, there is a marked phase separation into domains of different polarity. The domains having the highest polarity include water, which is made strongly acid by the $-\text{SO}_3\text{H}$ groups delimiting the domains. These high polarity domains are immersed in a low polarity matrix comprising the main perfluorinated chains and the perfluoroether side chains. Proton conduction occurs when different polar domains come into contact following fluctuations in the low polarity matrix. When this happens, there is long range migration of protons from one high polarity domain to another in the form of H_3O^+ ions. The perfluorinated copolymers described above characteristically have high proton conductivity and excellent chemical stability. On the other hand they are extremely expensive and only perform their function if they are suitably hydrated. Finally, perfluorinated copolymers do not always succeed in preventing the reagents from permeating from one electrode to another. The microscopic dynamics of the low and high polarity domains present in the perfluorinated copolymers are intimately associated. One consequence of this fact is that the maximum temperature at which a perfluorinated copolymer can operate efficiently is approximately 80-90°C; above this there are transitions which change the microscopic structure of

the material, causing it to dehydrate easily with a consequent fall in proton conductivity. One of the most important aims of research in the field of proton exchange membranes for use in PEMFC includes the use of non-humidified gaseous reagents at an operating temperature of at least 120-130°C. Under these conditions it is possible to design smaller and more compact PEMFC systems that are also capable of using, as a fuel, "dirty" hydrogen obtained from the processes of the steam reforming of hydrocarbons. Other families of proton conduction materials have also been conceived, these including polyethersulphone sulphonates, polyetherketone sulphonates, sulphonated silicones and others. Although in many respects better than perfluorinated copolymers, none of these materials are at present able to fully express their potential and still require appreciable research efforts.

One of the strategies for obtaining proton conduction membranes having better performance characteristics than that provided by the systems nowadays available is that of developing inorganic/organic hybrid membranes. These membranes comprise a material capable of conducting protons, such as for example Nafion, in which nanometric inorganic powders, such as oxides and phosphonates acting as fillers which may have been given surface functionality, are dispersed. The resulting inorganic/organic hybrid materials may be characterised by better mechanical properties than the proton-conducting starting material; their proton conductivity may be better and be less influenced by the level of hydration under which they operate.

Proton-conducting inorganic/organic hybrid membranes are well known in the art and are described for example in the following articles: Di Noto et al., *Journal of Power Sources*, 178 (2008) 561-574; Di Noto et al., *Journal of Power Sources*, 187 (2009) 57-66; Chen et al., *Journal of Membrane Science*, 307 (2008) 10-20; all of which are incorporated for reference.

Fuel cells containing ion-exchange membranes are also described in US7713899, US7661542 and US2008/0248356, all of which are included here for reference.

Another family of devices of great technological interest based on functional elements quite similar to those described above for applications in PEMFC is that of PEM electrolyzers (Proton Exchange Membrane electrolyzers). A PEM

electrolyser is essentially a PEM fuel cell which acts conversely by converting the electrical power and the water fed to it into hydrogen and oxygen having a high degree of purity (in excess of 99.9%) through an electrolysis process. PEM electrolyzers are used to produce pure gases only when they are needed for a particular application, thus avoiding the need to store them in heavy bulky cylinders subject to strict safety standards for high-pressure highly flammable gases. The core of a PEM electrolyser comprises the same proton exchange membrane as is used in a PEMFC; the material used to make the membrane must have optimum proton conductivity and high chemical and electrochemical stability.

PEM electrolyzers are well known in the art and are for example described in Spiegel, *Designing & Building Fuel Cells*, 2007, 346-348, McGraw-Hill and in Grot, *Fluorinated Ionomers*, 2008, 113-116, William Andrew Inc., all of which are included here for reference.

WO2005/090235 and WO2006/077203 describe the production of undoped titanium dioxide. Fluorine-doped titanium dioxide is described in: Li et al., *Journal of Fluorine Chemistry*, Elsevier, vol. 126, n. 1, 69-77, 2005; Todorova et al. *Material Science and Engineering*, Elsevier, vol. 152, n. 1-3, 50-54, 2008; Czoska et al. *Journal of Physical Chemistry*, vol. 112, 8951-8956, 2008; US5597515; WO 2009/113045.

Description of the invention

It has now been surprisingly found that an inorganic/organic hybrid membrane containing fluorine-doped TiO_2 according to this invention has better ion conductivity and mechanical properties than the inorganic/organic hybrid membranes known in the art.

Membranes containing fluorine-doped TiO_2 , which form the subject matter of this invention, can conduct protons but can also conduct ions other than protons (for example NR_4^+ , where R is a C_1 - C_6 alkyl radical, such as for example methyl or ethyl).

Also the proton conductivity and performance of inorganic/organic hybrid membranes containing such fluorine-doped TiO_2 in PEMFC fuel cells are less compromised by dehydration than similar systems which do not contain fluorine-

doped TiO₂.

In addition, use of the aforesaid membranes in the production of PEM electrolyzers provides these electrolyzers with a longer service life.

Finally, fluorine-doped TiO₂ may be functionalised with fused alkali metals or alkaline earth metals (for example Li or Na). The surface of the material obtained is functionalised with ions of the abovementioned metal and can be used to produce a solid-state electrolyte for ion batteries. In particular, through thermogravimetric analyses these new electrolytes show stability up to 250°C suggesting for example that they may be used in high temperature lithium batteries, with all the advantages associated with increased conductivity.

The present invention therefore relates to fluorine-doped TiO₂ and the corresponding process for its preparation.

For the purposes of the present invention the term *fluorine-doped TiO₂* means particles of said crystalline metal oxide having an average particle size of less than 500 nm, preferably between 10 and 500 nm, containing fluorine, hydroxy groups, ammonium cations and nitrogen oxides. In particular the terms *fluorine-doped TiO₂ particles*, *fluorine-doped titanium dioxide particles* or *FT* mean particles of anatase having an average particle size of less than 500 nm, preferably between 10 and 500 nm, even more preferably between 50 and 300 nm, which have fluorine, hydroxy groups, ammonium cations and nitrogen oxides on their surface.

More particularly said particles are of the "shell-core" type, that is they are formed of an internal core essentially comprising crystalline titanium dioxide, preferably anatase, and a surface coating having a mean thickness of between 0.3 and 20 nm, preferably between 0.6 and 10 nm. The surface coating contains fluorine atoms bridging with titanium atoms and terminal fluorine atoms; it is also rich in hydroxy groups, ammonium cations and nitrogen oxides located on the surface of the coating.

According to one of the aspects of the invention, the process for the production of fluorine-doped TiO₂ comprises the following stages:

- (a) a titanium ore, preferably containing iron, is reacted with a NH₄HF₂ aqueous solution;

- (b) the aqueous dispersion thus obtained is filtered with subsequent separation of a solid residue and an aqueous solution containing titanium salts;
- (c) the aqueous solution so obtained is subjected to hydrolysis, said hydrolysis comprising a first stage at pH 6.5-8.0 and a second stage at pH 9.0-11.0;
- (d) the aqueous dispersion thus obtained is filtered and the solid residue is subjected to pyrohydrolysis at a maximum temperature of approximately 500°C, preferably approximately 450°C;
- (e) optionally the filtrate obtained from stage (d) is heated to a temperature of 150-170°C, preferably approximately 160°C, and kept at this temperature for a period of 0.5 to 2 hours, with the consequent production of NH_4HF_2 , which once re-dissolved in water can be recycled to stage (a).

This process includes the extraction of titanium from the ilmenite ore (FeTiO_3), which may possibly be enriched; this extraction takes place within a suitable reactor, causing the ore to react with a concentrated aqueous solution of between 10% and 37% by weight and preferably approximately 30% by weight of NH_4HF_2 having a pH preferably between 5.5 and 5.7. Chemical analysis of the ilmenite performed using ICP-AES before the start of the reaction with NH_4HF_2 has shown that the ore contains traces (<1% by weight) of Al, Ca, Co, Ni and Zn. 1.1% by weight of W is also present.

The ore is added to the reactor preferably with an average particle size of 0.05-1.5 mm, even more preferably approximately 0.2 mm, and may be preheated to 80-120°C, preferably to approximately 100°C. It is suggested that the ore should be added to the base of the reactor by means of a system which prevents the gases present within the reactor from rising up the inlet pipe for the sand. The aqueous solution of NH_4HF_2 is preferably preheated to 50-100°C, preferably to approximately 80°C; the ratio by weight between the ilmenite and the NH_4HF_2 solution (preferably 30% by weight) is normally between 1:6 and 1:8, and is preferably approximately 1:7.5.

The reactor has equipment to stir the ilmenite sand in such a way as to encourage intimate contact between the reagents (ilmenite and solution), in particular at the bottom of the reactor. The stirring is possibly such as not to create turbulent motion in the top of the reactor; in the best embodiment the stirring speed should

not exceed 20 rpm, preferably 10 rpm.

The temperature within the reactor is kept at 100-110°C, preferably 104-106°C, and even more preferably approximately 105°C, at a pressure of between approximately 1 and 2 bar; this may be achieved using the conventional means known in the art, for example a heating jacket system on the outside of the reactor; in the best embodiment the greatest quantity of heat is transmitted through the bottom of the reactor, where the concentration of reagents is highest; also, in order to prevent the escape of gaseous compounds into the outside environment, it is recommended that a leaktight reactor should be used. The reaction has a preferred duration of 40 to 80 minutes.

The pH within the reactor under these operating conditions is approximately 6.5-7.0.

Gaseous ammonia is produced by the reaction; this can be conveyed outside the reactor and absorbed in water to obtain a concentrated solution (approximately 24% by weight) of ammonium hydroxide NH_4OH , which can in turn be used during the subsequent stages of hydrolysis of the titanium salts. Removal of the ammonia also makes it possible to control the pressure within the reactor (normally approximately 1 bar).

The reaction between FeTiO_3 and NH_4HF_2 (in aqueous solution) produces two salts: ammonium hexafluorotitanate $(\text{NH}_4)_2\text{TiF}_6$ and ammonium (ferric) hexachloroferrate $(\text{NH}_4)_3\text{FeF}_6$. The titanium salt has a solubility which depends directly on temperature and is inversely dependent on the concentration of NH_4HF_2 ; it therefore remains in solution under the reaction conditions. The iron salt instead has negligible solubility and remains in the form of a solid dispersion.

An aqueous solution of NH_4HF_2 and $(\text{NH}_4)_2\text{TiF}_6$ containing the dispersed $(\text{NH}_4)_3\text{FeF}_6$ salt is recovered from the reactor. The dispersion leaving the reactor is made to pass through a filter capable of retaining solid particles having dimensions between 0.1 and 2.0 μm ; this result can be achieved using meshes having holes of 2-3 nm, preferably approximately 2.5 nm. In this section the solid dispersion of the iron salt is separated from the solution of titanium salt.

The filtered sludge may be further washed with NH_4F and/or NH_4HF_2 solutions and then filtered a second time; these two filtrations may take place within the

same filtering equipment.

After filtering the following is obtained:

- (a) a solid sludge portion containing the iron salt $(\text{NH}_4)_3\text{FeF}_6$;
- (b) an aqueous solution containing the titanium salt $(\text{NH}_4)_2\text{TiF}_6$, ammonium difluoride (NH_4HF_2) and traces of the iron salt $(\text{NH}_4)_3\text{FeF}_6$, which is a contaminant for the final product.

The solid sludge portion (a) normally has a moisture content of between 10 and 20% by weight depending upon the filtering equipment used. The aqueous solution (b) normally has an iron salt $(\text{NH}_4)_3\text{FeF}_6$ content of approximately 0.04-0.06% by weight.

The aqueous solution (b) from the filtration stage is then further purified from the iron salt $(\text{NH}_4)_3\text{FeF}_6$ in order to reduce its concentration to less than 0.01% by weight, preferably less than 0.001% (understood as the concentration of the iron salt), which is equivalent to approximately 2.5 mg/L (2.5 ppm) of Fe ions in solution.

This is achieved about by displacing the pH of the solution to 6.5-8.0, preferably to 7.0-8.0 and even more preferably to 7.0-7.5 by adding concentrated ammonium hydroxide (NH_4OH) solution (approximately 24% by weight); this operation causes the formation of an insoluble ammonium oxyfluorotitanate $[(\text{NH}_4)_3\text{TiOF}_5]$ which precipitates incorporating the residual iron salt $(\text{NH}_4)_3\text{FeF}_6$. The operation is performed within a reactor at a temperature of 50-70°C, preferably approximately 60°C, with stirring; the stirring speed is normally 40-90 rpm, preferably approximately 50 rpm; the quantity of NH_4OH which has to be added is controlled by keeping the pH in the outflow from the vessel to a preferred value of 7.0-8.0, and even more preferably 7.5-8.0.

The dispersion is filtered, yielding an aqueous solution of the titanium salt $(\text{NH}_4)_2\text{TiF}_6$, further purified from compounds containing iron, and a sludge containing the titanium complex and the iron salt $(\text{NH}_4)_3\text{FeF}_6$.

The sludge may be dissolved again within a further vessel provided with stirring for acidification; this takes place with the addition of a concentrated NH_4F and/or optionally NH_4HF_2 solution (approximately 40-50% by weight) to a pH of approximately 6.5-7.0; in this way the titanium salt becomes soluble again,

forming $(\text{NH}_4)_2\text{TiF}_6$. The solution/dispersion so obtained is then recycled in addition to the outflow from the main reactor.

This solution/dispersion contains both the soluble titanium salt $(\text{NH}_4)_2\text{TiF}_6$ and the insoluble iron salt $(\text{NH}_4)_3\text{FeF}_6$ which has been incorporated by the ammonium oxyfluorotitanate as it precipitates out. This makes it possible to recover both metals completely without producing any waste.

The purified solution, which contains the titanium salt $(\text{NH}_4)_2\text{TiF}_6$, NH_4F and water, is then subjected to further hydrolysis.

The further hydrolysis is performed in a reactor fitted with a stirrer (approximately 10 rpm), maintaining a temperature of 50-70°C, preferably approximately 60°C. The reaction takes place by raising the pH of the solution to very high values, preferably 9-11 and even more preferably approximately 10-11 (monitoring the outflow from the reactor); this result is obtained by adding a concentrated solution of ammonium hydroxide NH_4OH (approximately 24% by weight); this ammonium hydroxide solution is preferably used in large excess compared to that which is required for the reaction.

The further hydrolysis brings about the precipitation of a mixture of hydrated titanium salts and oxides $(\text{NH}_4)_2\text{TiOF}_4 + (\text{NH}_4)_3\text{TiOF}_5 + \text{TiO}_2 \cdot n \text{H}_2\text{O}$ in the form of particles having dimensions of approximately 0.01 μm . As a consequence an aqueous solution of NH_4F with a dispersed solid comprising salts which can be filtered out is produced in the hydrolysis reactor.

The dispersion thus obtained is then filtered through a filter having extremely fine meshes (2-3 nm, preferably approximately 2.5 nm).

The solution leaving the filter, which contains NH_4F , water, excess ammonia and traces of titanium salts, is preferably treated to obtain solid NH_4HF_2 so that it can be reused in the stage of reacting with the ilmenite.

In order to perform this operation, the solution is preferably heated to boiling in the presence of very slight negative pressure (10 to 60 mm of Hg) with the release of ammonia; the temperature is then raised to 150-170°C and kept there for at least 60 minutes (still under negative pressure), preferably for 60-120 minutes, with consequent decomposition of the NH_4F salt into NH_4HF_2 and ammonia, with the latter being removed. After this operation a solid salt is present in the bottom

of the reactor and this is dissolved in water to yield a solution of 10% to 37% by weight, preferably approximately 30% by weight, having a pH of 5.5-5.7.

The sludge part leaving the filter, which normally has a moisture content of between 10 and 20% by weight depending upon the filtering equipment, is subjected to a pyrohydrolysis process. In more detail, after drying to the point where water is removed, the sludge containing the titanium salts undergoes pyrohydrolysis at a maximum temperature of 500°C, preferably at a maximum temperature between 330 and 470°C and even more preferably between 350 and 450°C, being kept at the maximum temperature for a period of 1-3 hours, preferably approximately 2 hours; this normally takes place in a furnace in an atmosphere of superheated steam; the maximum temperature is reached gradually, preferably with a gradient of 3-6°C/minute, even more preferably 5°C/minute.

The gaseous compounds extracted from the furnace containing NH_3 , HF, H_2O are normally cooled and absorbed in water to obtain a concentrated solution of NH_4F and/or NH_4HF_2 which can easily be recycled and reused to charge the reactor. It is recommended that the gases should not be cooled below 200°C before being absorbed in water, to prevent the formation of NH_4F and/or NH_4HF_2 crystals with consequent obstruction of the tubing.

Under these conditions, if the metal is titanium, all the ammoniacal fluorine bonds are broken, yielding a powder product comprising just fluorine-doped TiO_2 particles, the characteristics of which are listed below:

- Analysis by HR-TEM (*High-Resolution Transmission Electron Microscopy*) reveals the sub-micron morphology of the FT powders. In particular the particles are found to have a polydisperse size distribution, being present either as regular shapes with well-defined edges or as smaller-size irregular shapes. Measurement of the interplanar distances for both types of particles shows that nanocrystals of anatase having dimensions of less than 500 nm are present (see Figures 1 and 2).
- Scanning electron microscope (SEM) analyses made using an acceleration voltage of 10 kV and a standard secondary electrons detector have revealed that some of the particles have aggregated to form globular masses while some have aggregated to form internally hollow octahedral structures having edges

of variable length between 40 to 60 μm , preferably approximately 50 μm (see Figures 3 and 4).

- Elementary analysis using SEM with energy dispersion microanalysis (*SEM-EDS*) has revealed a quantity by weight of fluorine (with respect to the total mass of the particles) of between 0.5 and 5% by weight, preferably between 1.0 and 4% by weight.
- XPS (*X-ray Photoelectron Spectroscopy*) surface elementary analysis has revealed a quantity of fluoride of between 9% and 30% molar with respect to the titanium, which is approximately equivalent to a weight fraction of fluorine of between 1.5 and 9% by weight, preferably between 2.1 and 6.8% by weight. The latter values are slightly greater than those obtained using the scanning electron microscope (SEM), an indication that the crystalline structures which are richer in fluorine and other elements (nitrogen and hydroxy groups) are to be found on the surface.
- Elementary analysis has revealed a quantity of nitrogen of between 0.2 and 8% by weight, preferably between 0.3 and 7.5%, even more preferably between 2.5 and 7%, and a quantity of hydrogen between 0.05 and 4% by weight, preferably between 0.08 and 3%, even more preferably between 1.5 and 2.5% (the percentages are to be understood as being relative to the total mass of the particles); the presence of hydrogen has been associated with the surface hydroxy groups, while the nitrogen has been associated with ammonium groups, NH_4 , and nitrogen oxides, NO_x , above all on the surface.
- Chemical analysis of the particles performed using ICP-AES has shown that they contain traces (<1% by weight) of Ca, Co, Fe, K, Mg, Nb, Ni, W, Si and Zn;
- X diffraction (XRD) investigations have confirmed that the FT particles are made of a single crystalline phase - anatase, without amorphous traces or traces of the initial transition to rutile. No structural modification due the presence of the fluoride was noted from the XRD spectrum of the FT powders and it can therefore be assumed that this is only present on the surface of the FT particles.

From all the investigations it follows that the particles are nanocrystals of titanium dioxide containing fluorine, preferably anatase, said nanocrystals being characterised in that the fluorine is mainly present on their surfaces and that its concentration decreases gradually moving away from the surface, that is towards the centre of the crystal.

One aspect of the invention is therefore represented by the fact that the fluorine (or the fluorine atoms) is essentially present on the surface of the particles; in other words at least 80% of the fluorine, preferably at least 90%, is present in a surface layer of the particles, this surface layer having a mean thickness of between 0.3 and 20 nm, preferably between 0.6 and 10 nm.

The investigations performed also demonstrate that the fluorine atoms both form bridges between titanium atoms and are terminal.

Hydroxy groups as well as ammonium cations and nitrogen oxides are also present on the surfaces of the particles.

The "shell-core" structure of the particles, that is the surface location of the fluorine and the hydroxy groups, has a significant part to play for the purpose of using these in the production of inorganic/organic hybrid membranes and/or in the production of solid-state electrolytes.

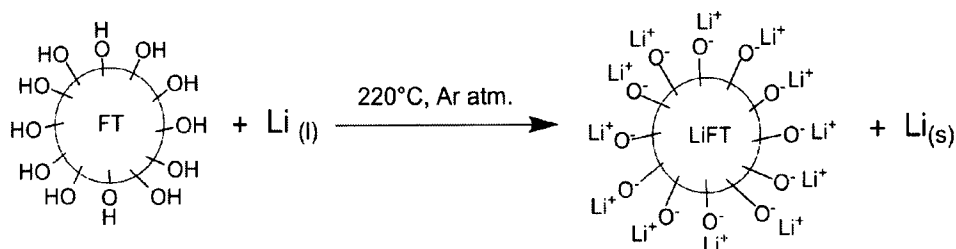
The inorganic/organic hybrid membrane is prepared from a uniform dispersion in a suitable solvent which includes the proton-conducting material and the filler in the quantities established through a conventional solvent-casting process described for example in Liao *et al.*, "Fabrication of porous biodegradable polymer scaffolds using a solvent merging/particulate leaching method", *Journal of Biomedical Materials Research* **59** (4): 676–81, March 2002, included here for reference. The hybrid membrane is obtained after the solvent has been removed and the resulting system has been suitably modelled. At this point the membrane may undergo a number of thermal, mechanical and chemical treatments to consolidate it and improve its mechanical and functional properties. The membrane is finally washed and suitably activated to remove any traces of solvent and other undesirable anionic and cationic contaminants and if possible improve its mechanical and functional properties further, thus giving rise to the final inorganic/organic hybrid membrane.

The solvent casting process mentioned may be performed from liquid suspensions or homogeneous liquid solutions at temperatures varying between 0 and 170°C, said suspensions and liquid solutions being preferably obtained by mechanical mixing and by the treatment of precursors and solvents with ultrasound; preferably ionomer polymers based on polytetrafluoroethylene sulphonates, polysulphone sulphonates, polyetherketone sulphonates, acidified polybenzimidazoles, polyalkyl siloxanes rendered functional with acid groups and aprotic polar organic solvents such as DMF are preferably used.

Alternatively the membranes according to this invention may be obtained by other conventional processes, for example by extruding mixtures of precursors at temperatures over 150°C.

The solid-state electrolyte may be prepared by reacting the aforesaid particles in the anhydrous state with an alkali or alkaline earth metal, preferably lithium, in the fused state. Said metal in the fused state is preferably used in excess with respect to the particles; preferably the metal is used in a quantity of between 1000 and 0.5 parts by weight to one part by weight of particles, even more preferably in quantities between 50 and 1 part by weight per one part by weight of particles.

The lithiation reaction of fluorine-doped titanium dioxide particles may be shown diagrammatically as follows.



As will be seen, the reaction leads to the formation of particles having alkali or alkaline earth metal cations on its surface, in the case in point Li^+ . The new compound will be indicated below as LiFT.

The following examples are illustrative and do not restrict the invention.

EXAMPLES

Example (a): preparation of fluorine-doped TiO_2 (FT)

7 litres of water, 3 kg of NH_4HF_2 salt and 1341 g of ilmenite sand sieved to a particle size of less than 200 microns were placed in a stirred reactor having a

volume of approximately 10 litres. The mixture was then brought to boiling at atmospheric pressure, and kept there for approximately 1 hour. After this stage of reaction with the ore, 4 litres of solution were drawn off through the valve in the bottom of the reactor and then filtered. 1.5 litres of a concentrated 30% ammonia solution was added to the solution thus filtered containing the titanium and iron fluoride salts, thermostatted to 70°C, increasing its pH to 7.3. The white precipitate was separated out by filtration and a further 2 litres of a concentrated solution of 30% ammonia were added to the filtrate to obtain a pH of around 9.5. The white precipitate was separated out by filtration and subjected to the subsequent stage of pyrohydrolysis. Approximately 30 g of this wet intermediate (moisture content approximately 20%) was placed in an aluminium tube. The tube was inserted into a furnace chamber. It was then heated as follows: 4.7°C/min up to 450°C and kept there for 2 hours. Slow cooling followed. Approximately 20 g/min of steam were fed to the tube during the entire test until it ceased to remain at high temperature. The final powder was yellow in appearance and not agglomerated. This comprised anatase doped with approximately 2.3% by weight of fluorine.

Example (b): membranes containing fluorine-doped TiO₂

This example provides a detailed description of the preparation and investigation of some inorganic/organic hybrid membranes containing fluorine-doped TiO₂ according to the present invention. The mechanical properties of the membranes were studied by dynamic-mechanical analysis (DMA); the membranes were also used to build individual fuel cells tested under different operating conditions for reagent pressure, relative humidity and oxidising agent used.

Membrane preparation

A quantity of 5% by weight Nafion™ emulsion was dried by evaporating the solvents. The quantities of solid obtained were dissolved in approximately 15 ml of dimethylformamide in the ratios shown in Table 1; the product was a mixture which was rendered homogeneous following treatment in a conventional ultrasound bath lasting 2 hours. The filler, comprising sub-micron particles of fluorine-doped TiO₂ obtained according to example (a) were added to the Nafion mixture, achieving the filler/Nafion ratio by weight shown in Table 1. The

resulting suspension was carefully homogenised by treatment in an ultrasound bath for 5 hours and was then subjected to a conventional solvent-casting process in dry air to remove the solvent completely. The membrane obtained was: a) hot pressed at a temperature below 150°C; b) repeatedly washed with hydrogen peroxide to remove any traces of organic solvent; c) repeatedly activated with a solution of sulphuric acid to expel cationic contaminants and activate the sulphone groups of the Nafion. The final inorganic/organic hybrid membrane was obtained by drying the product obtained in air.

Table 1

Quantity of Nafion and filler used in membrane preparation				
Membrane	Nominal % weight of filler	Mass of Nafion (mg)	Mass of filler (mg)	Effective % weight of filler
Nafion	0	1040.4	0	0
TiO ₂ F 5%	5	982.6	43.9	4.28
TiO ₂ F 10%	10	936.4	89.7	8.74
TiO ₂ F 15%	15	884.3	135.4	13.3

The filler used in the preparation of inorganic/organic hybrid membranes is indicated in Table 1 by the formula TiO₂F. Four membranes in all were prepared. Three of these were inorganic/organic hybrid membranes characterised by different percentages by weight of TiO₂F; the fourth membrane did not contain inorganic filler and was used as a reference. All the resulting membranes were of similar thickness, approximately 0.1 millimetres.

Dynamic-mechanical analyses

The membranes obtained were subjected to dynamic-mechanical analyses (DMA). Figure 5 shows the change in the elastic modulus of the membranes as a function of temperature. It can be seen that all the inorganic/organic hybrid membranes are characterised by decidedly better mechanical properties than the pure Nafion membrane used as a reference. In particular, as shown in insert a) in Figure 5, at 25°C the elastic modulus of all the inorganic/organic hybrid

membranes is almost twice that of the pure Nafion membrane. It can also be noted that while the 5% TiO_2F membrane and the pure Nafion membrane undergo irreversible elongation at temperatures above approximately 120°C , the 10% TiO_2F and 15% TiO_2F membranes maintain their mechanical properties at quite high temperatures, up to and beyond 200°C . Figure 6 shows the change in $\tan \delta$ = viscous modulus/elastic modulus of the membranes in relation to temperature. The maximum for peak α decreases substantially as the quantity of filler included in the inorganic/organic hybrid membrane increases, as shown in insert a). This experimental evidence is indicative of how the relaxation α , which is responsible for the decline in the mechanical properties of pure Nafion at $T > 100^\circ\text{C}$, is strongly inhibited by the presence of the filler. As a consequence the inorganic/organic hybrid membranes described in this example may also be used at higher temperatures than pure Nafion, beyond $120\text{-}130^\circ\text{C}$, while continuing to maintain their mechanical properties.

Determination of the performance of the membranes in an individual PEMFC

The membranes described in this example were used to manufacture membrane-electrode assemblies (MEA) which were then tested under operating conditions as individual PEMFC. The MEA were prepared using standard procedures. All the MEA used electrodes prepared from porous Teflon-coated carbon paper provided with microporous layers. Catalysts containing 20% by weight of platinum in the form of nanometric particles supported on activated carbon were used. The overall platinum load used for all the electrodes was 0.4 mg/cm^2 . The active area of each electrode was approximately 4 cm^2 . Figure 7 shows the polarisation curves for the MEA assembled from the membranes described in this example. It can be seen how all the MEA assembled from inorganic/organic hybrid membranes have better performance characteristics than the MEA assembled using the pure Nafion membrane. The gradient of the polarisation curve of a PEMFC fed with hydrogen at a cell voltage of approximately 0.6 V is inversely correlated to the proton conductivity of the membrane used. In general, the steeper the slope, the poorer the proton conductivity of the material from which the membrane is made. It can therefore be deduced that under "ideal" conditions (high reagent pressure, $P = 5$

bar, use of oxygen as an oxidising agent, 100% relative humidity and $T = 85^{\circ}\text{C}$) all the inorganic/organic hybrid membranes have greater proton conductivity than the pure Nafion. This conclusion remains valid even if the MEA are subjected to a lower reagent pressure ($P = 2$ bar, Figure 8), and when the MEA are fed with air instead of pure oxygen as an oxidising agent. The better performance of the inorganic/organic hybrid membranes than pure Nafion membrane is also evidenced by the higher maximum power density which can be obtained from the MEA, which is shown in Figure 9 and Figure 10 for reagent pressures of 5 and 2 bar, respectively. All the MEA were also tested under relative humidity conditions of 75%, 50%, 25%, 12.5% and 5%, maintaining a reagent pressure of 2 bar. Figure 11 shows the corresponding polarisation curves for the MEA assembled from pure Nafion membrane. Figure 12, Figure 13 and Figure 14 show the similar polarisation curves for the MEA assembled from 5% TiO_2F , 10% TiO_2F and 15% TiO_2F membranes, respectively. One way of evaluating the effect of relative humidity on the performance of MEA is that of using, as a parameter, the maximum power density provided by the device under various conditions, as shown in Figure 15. It can be seen how all the MEA have performances which worsen as the relative humidity of the reagents falls. However the MEA assembled using 10% TiO_2F membrane according to this invention is less influenced by dehydration than that assembled from pure Nafion membrane, above all if fed with pure oxygen as the oxidising agent.

Example (c): solid-state electrolyte

A quantity of FT obtained as in example (a) was rendered anhydrous under vacuum for 72 hours at 100°C and 10^{-1} mbar. 2 g of FT were reacted with a large excess of fused lithium at 220°C using an isomantle and mixing constantly. The reaction was performed in a crucible in an atmosphere of argon (oxygen and water < 1 ppm). FT and fused lithium metal were reacted for 2 hours. During the course of the reaction it was noted that the fluorinated titanium dioxide changed its colour from straw yellow to blue, retaining its appearance as a powder. The product was copiously washed (total 700 ml) with ethanol, obtaining the final product known as LiFT. ICP-AES analyses revealed that the LiFT had the

following composition Ti 33.8%, C 0.30%, N 0.37%, H 0.26% Li 1.34% and O 62.73% and SEM-EDS showed the fluorine content to be approximately 1.2% by weight.

Brief description of the Figures

Fig. 1-2. HR-TEM (*High-Resolution Transmission Electron Microscopy*) analyses of fluorine-doped titanium dioxide particles.

Fig. 3-4. Scanning electron microscope (SEM) analyses of fluorine-doped titanium dioxide particles.

Fig. 5. Change in the elastic modulus of the membranes in relation to temperature. The values of the elastic modulus at 25°C are shown in insert a).

Fig. 6. Change in $\tan \delta$ = viscous modulus/elastic modulus with temperature for the membranes. Insert a) shows the values of $\tan \delta$ for the maximum peak α .

Fig. 7. Polarisation curves for MEA assembled from the membranes. The operating conditions are as follows: cell temperature 85°C; temperature of the hydrogen flow and oxidising agent flow 85°C; relative moisture content of the reagents 100%; flow of hydrogen: 800 sccm; oxidising agent used: air (top), pure oxygen (bottom); flow of oxidising agent: 1700 sccm (air), 500 sccm (pure oxygen); reagent pressure: 5 bar.

Fig. 8. Polarisation curves for MEA assembled from the membranes. The reagent pressure is 2 bar; the other operating conditions are the same as those shown in the description for Fig. 7.

Fig. 9. Maximum power density provided by MEA assembled from the membranes. Reagent pressure 5 bar, relative humidity of the reagents 100%. The remaining operating conditions are the same as those shown in the description for Fig. 7.

Fig. 10. Maximum power density provided by MEA assembled from the membranes. Reagent pressure 2 bar, relative humidity of the reagents 100%. The remaining operating conditions are the same as those shown in the description for Fig. 7.

Fig. 11. Polarisation curves for the MEA assembled from the pure Nafion

membrane with varying relative humidity of the reagents. Reagent pressure 2 bar; the other operating conditions are the same as those shown in the description for Fig. 7.

Fig. 12. Polarisation curves for the MEA assembled from 5% TiO_2F membrane with varying relative humidity of the reagents. Reagent pressure 2 bar; the other operating conditions are the same as those shown in the description for Fig. 7.

Fig. 13. Polarisation curves for the MEA assembled from 10% TiO_2F membrane with varying relative humidity of the reagents. Reagent pressure 2 bar; the other operating conditions are the same as those shown in the description for Fig. 7.

Fig. 14. Polarisation curves for the MEA assembled from 15% TiO_2F membrane with varying relative humidity of the reagents. Reagent pressure 2 bar; the other operating conditions are the same as those shown in the description for Fig. 7.

Fig. 15. Change in the maximum power density provided by the various MEA in relation to relative humidity at a reagent pressure of 2 bar. The other operating conditions are the same as those shown in the description for Fig. 7.

CLAIMS

1. Crystalline titanium dioxide particles having an average particle size of less than 500 nm and a fluorine content of between 0.5 and 5% by weight, preferably between 1.0 and 4%.
2. Particles according to claim 1, characterised in that they have an average particle size of between 10 and 500 nm, preferably between 50 and 300 nm.
3. Particles according to claim 1, characterised in that they contain hydroxy groups, ammonium cations and nitrogen oxides.
4. Particles according to claim 1, characterised in that they have a nitrogen content of between 0.2 and 8% by weight, preferably 0.3 and 7.5%, even more preferably between 2.5 and 7%, and a hydrogen content of between 0.05 and 4% by weight, preferably between 0.08 and 3%, even more preferably between 1.5 and 2.5%.
5. Particles according to claim 1, characterised in that the fluorine is essentially present on their surfaces.
6. Particles according to claim 1, characterised in that at least 80% of the fluorine, and preferably at least 90%, is present in a surface layer on the same, said surface layer having a mean thickness of between 0.3 and 20 nm, preferably between 0.6 and 10 nm.
7. Particles according to either of claims 5 or 6, characterised in that hydroxy groups are present on their surfaces.
8. Particles according to claim 1, characterised in that the titanium dioxide is in the form of anatase.
9. Process for the production of crystalline titanium dioxide containing fluorine atoms, comprising the following stages:
 - (a) a titanium ore containing iron is reacted with a NH_4HF_2 aqueous solution;
 - (b) the aqueous dispersion thus obtained is filtered with consequent separation of a solid residue and an aqueous solution containing titanium salts;
 - (c) the aqueous solution thus obtained is subjected to hydrolysis, this hydrolysis comprising a first stage at pH 6.5-8.0 and a second stage at pH 9.0-11.0;
 - (d) the aqueous dispersion thus obtained is filtered and the solid residue is

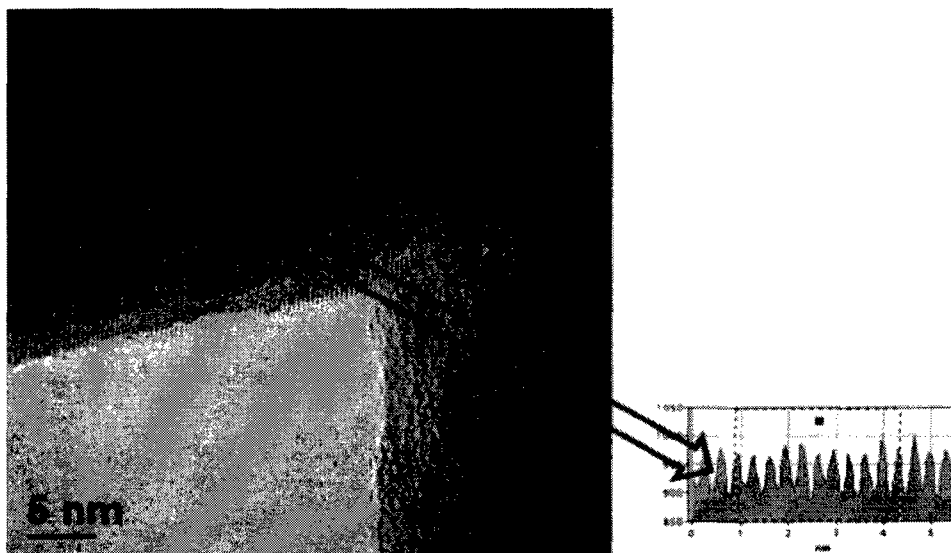
subjected to pyrohydrolysis at a maximum temperature of around 500°C, preferably approximately 450°C.

10. Process according to claim 9, characterised in that stage (a) is performed at 100-110°C, preferably at 104-106°C, even more preferably at approximately 105°C, and/or for a period of between 40 and 80 minutes.
11. Process according to claim 9, characterised in that stage (a) is performed at a pressure of approximately 1-2 bar and/or at a pH of approximately 6.5-7.0.
12. Process according to claim 9, characterised in that said NH_4HF_2 aqueous solution has a concentration of between 10% and 37% by weight, preferably approximately 30% by weight.
13. Process according to claim 9, characterised in that the filtration described in stages (b) and/or (d) is performed using meshes having holes of 2-3 nm, preferably approximately 2.5 nm.
14. Process according to claim 9, characterised in that hydrolysis (c) is performed through the addition of a solution of ammonium hydroxide.
15. Process according to claim 9, characterised in that hydrolysis (c) is performed with stirring, the first stage at a speed of 40-60 rpm, preferably approximately 50 rpm, and/or the second stage at approximately 10 rpm.
16. Process according to claim 9, characterised in that the first stage of hydrolysis (c) is performed at a pH of approximately 7.0-8.0 and/or in that the second stage of hydrolysis (c) is performed at a pH of approximately 10-11.
17. Process according to claim 9, characterised in that said pyrohydrolysis (d) is performed at a maximum temperature of 330-470°C, preferably 350-450°C.
18. Process according to claim 9, characterised in that the pyrohydrolysis (d) is performed for a period of 2-6 hours, preferably approximately 5 hours.
19. Process according to claim 9, characterised in that said pyrohydrolysis (d) is performed with the maximum temperature being maintained for approximately 1-3 hours, preferably approximately 2 hours,.
20. Process according to claim 9, characterised in that the solid residue from stage (b) is subjected to pyrohydrolysis at a maximum temperature of 450°C, preferably at 340-400°C, even more preferably at approximately 360-380°C, and preferably for 2-4 hours, even more preferably for approximately 3 hours.

21. Process according to claim 9, characterised in that it comprises a further stage (e) in which the filtrate obtained from stage (d) is heated to a temperature of 150-170°C, preferably approximately 160°C and is kept at that temperature for a period of between 0.5 and 2 hours, consequently obtaining NH_4HF_2 which once re-dissolved in water can be recycled to stage (a).
22. Titanium dioxide obtainable by the process according to any one of claims 9 to 21.

Figure 1

HR-TEM image

Figure 2

Detail of the HR-TEM image, showing the interplanar distances of the nanocrystals of anatase in FT, equal to 2.4 Å.

Figure 3

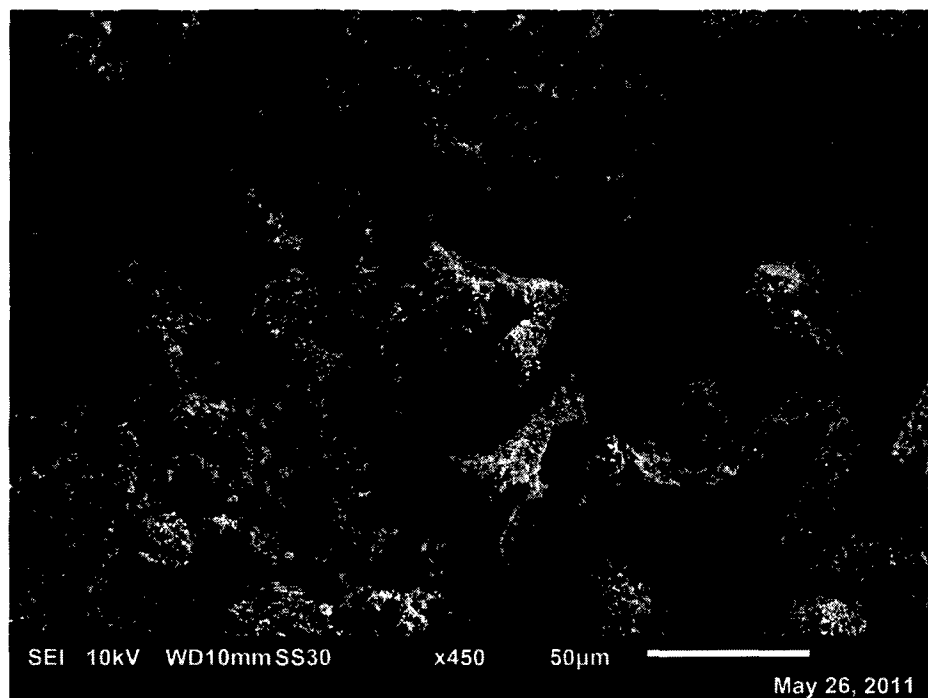


Figure 4

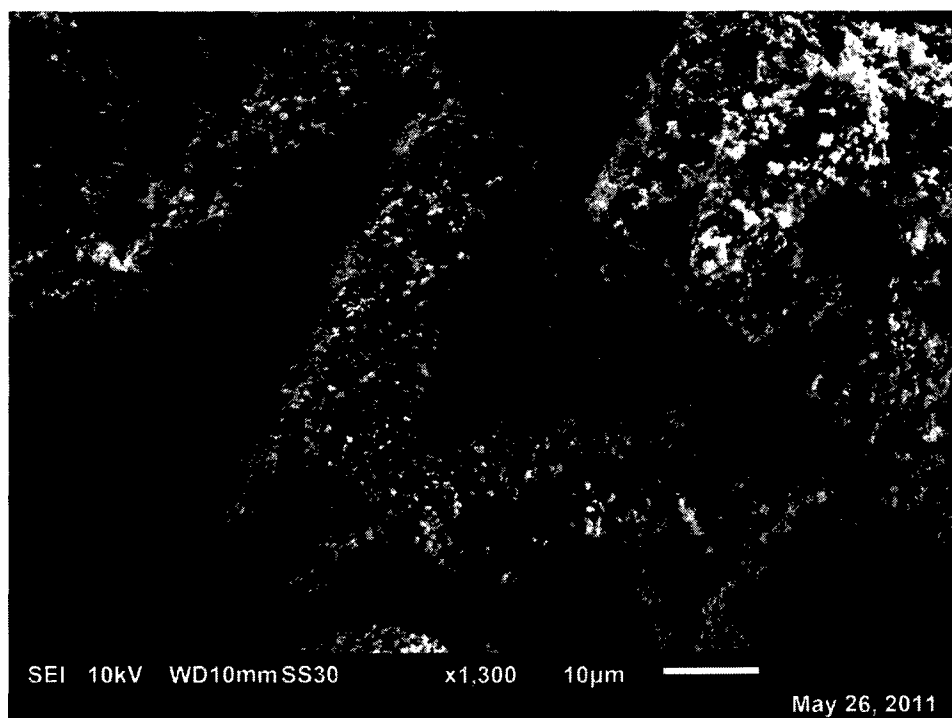


Figure 5

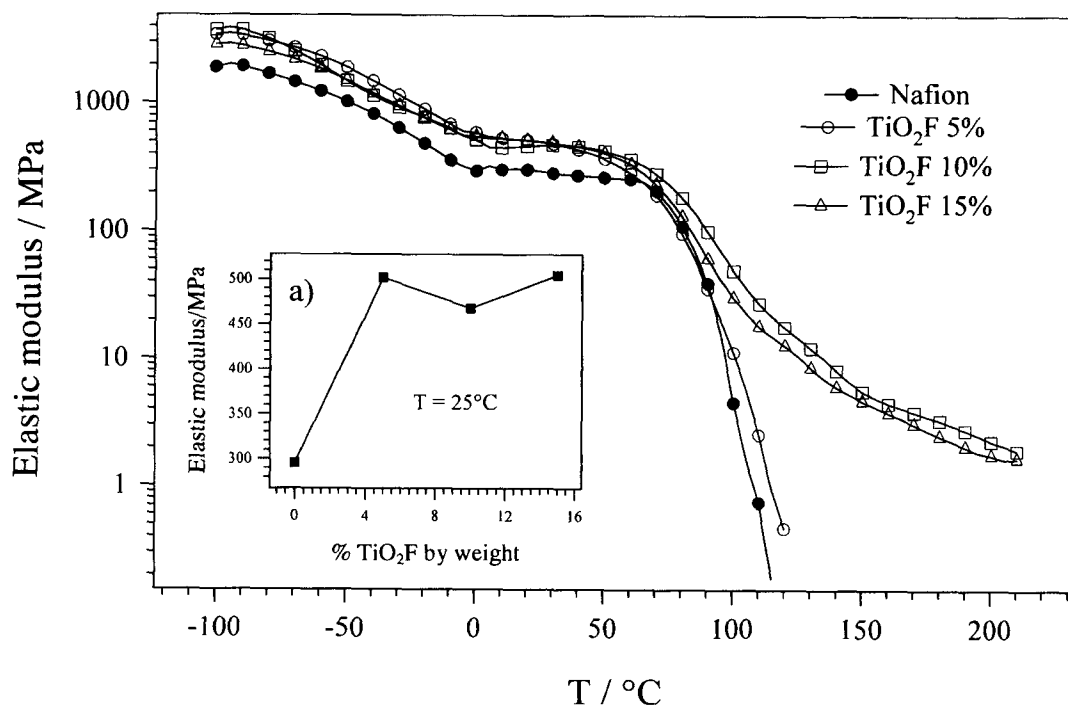


Figure 6

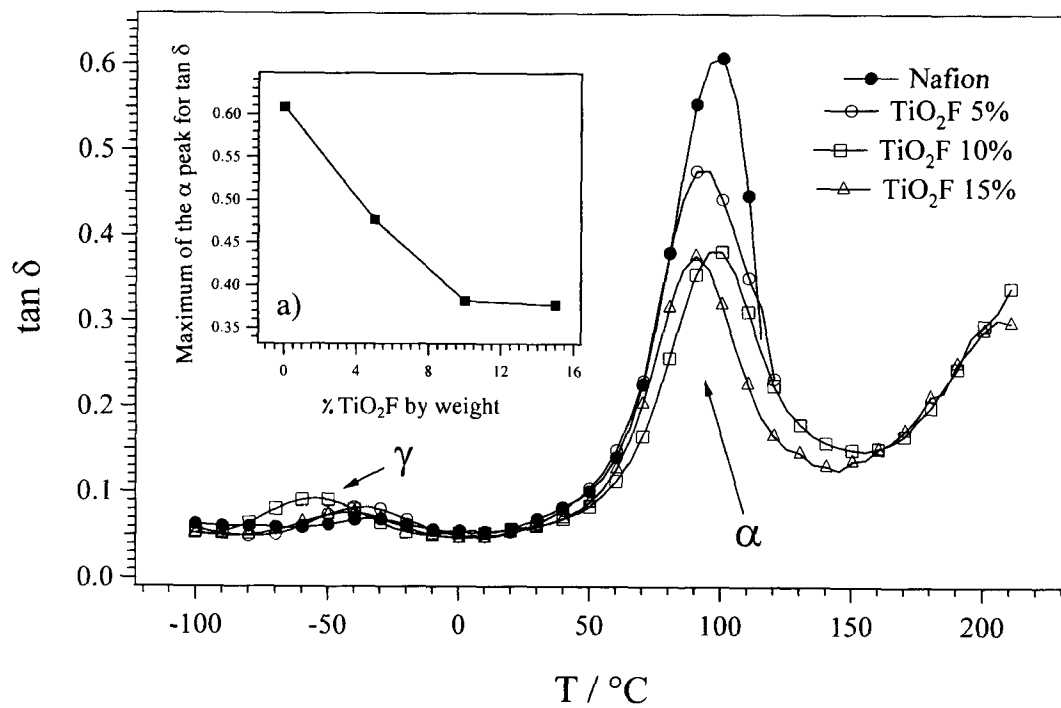


Figure 7

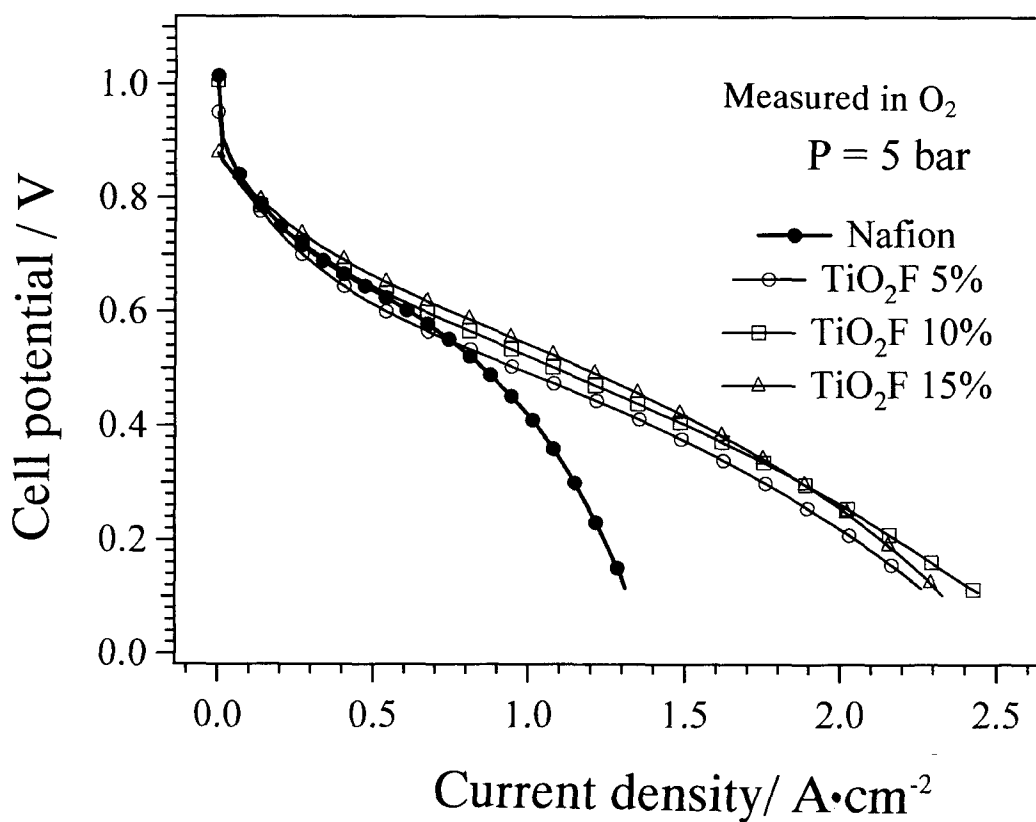
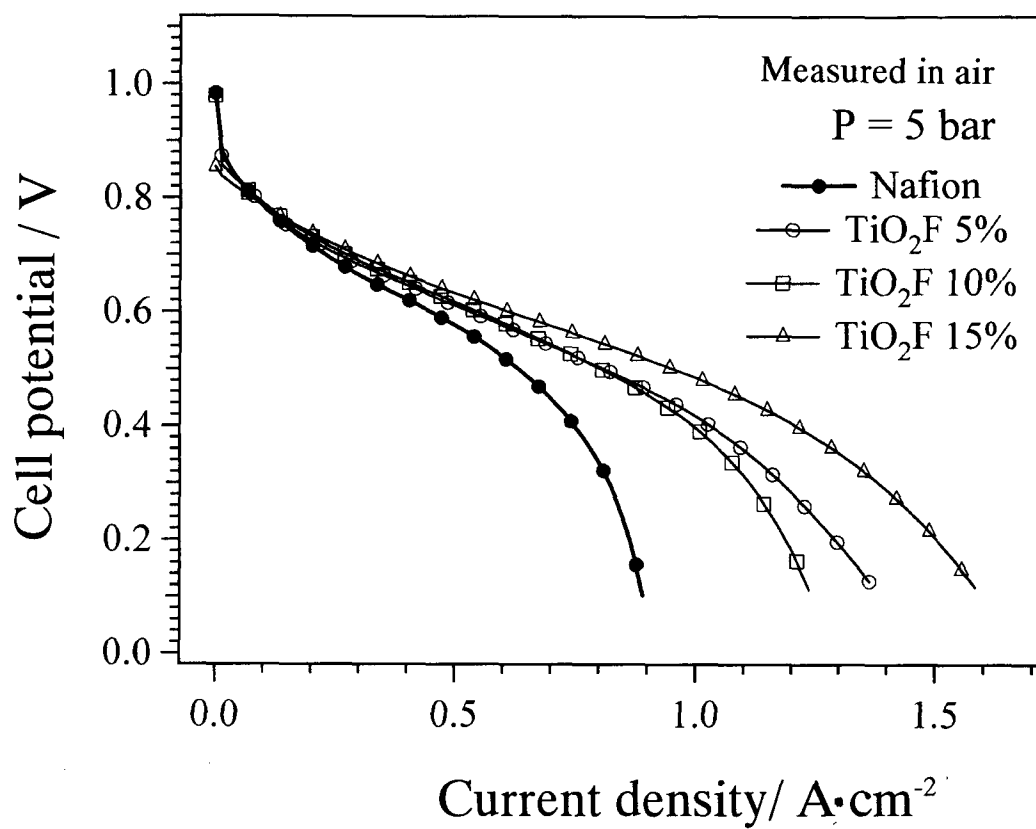


Figure 8

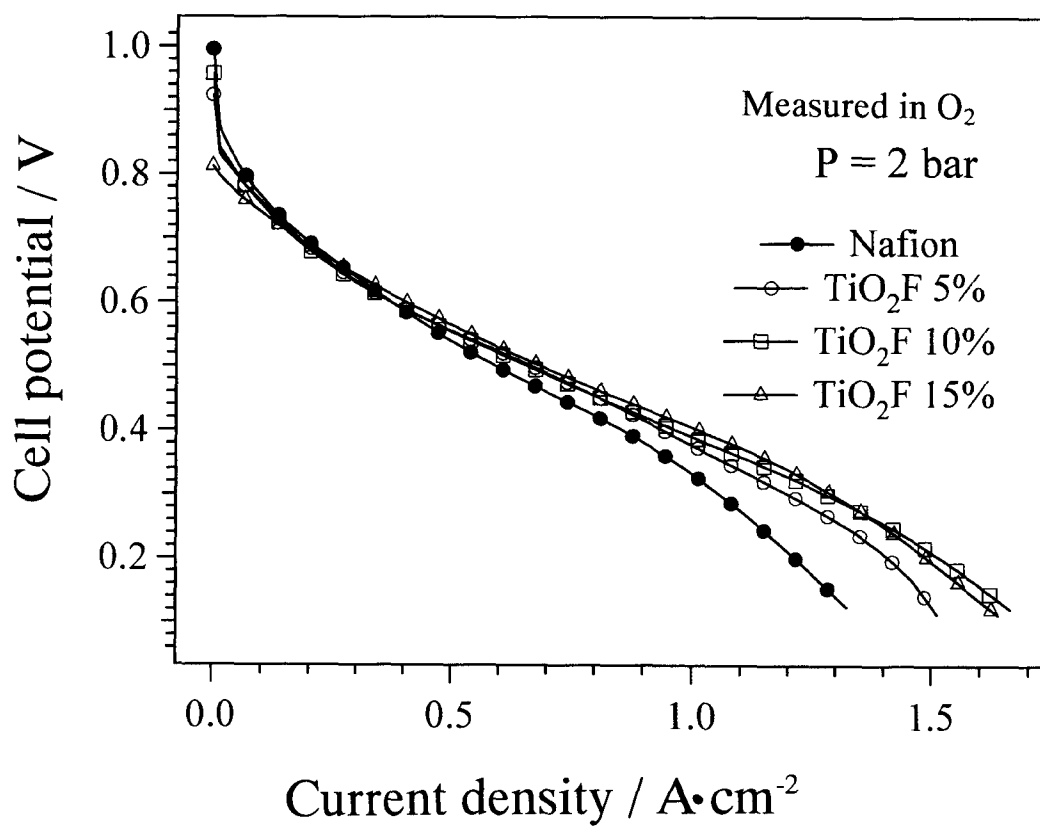
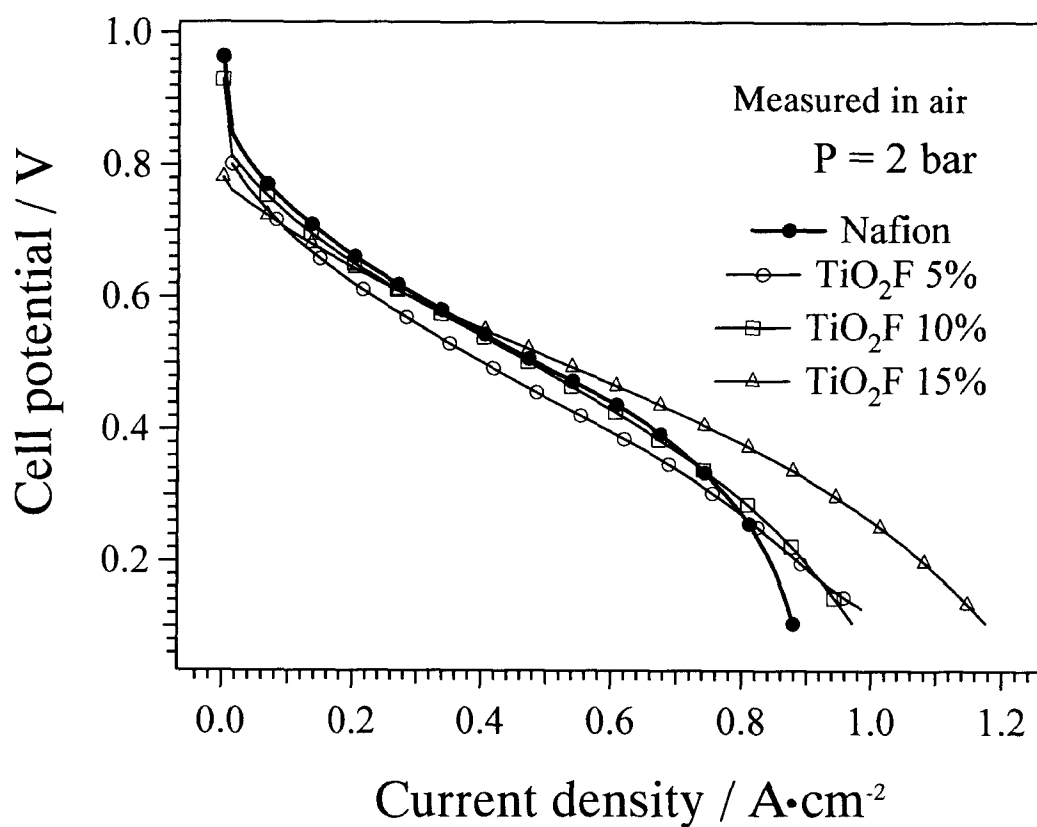


Figure 9

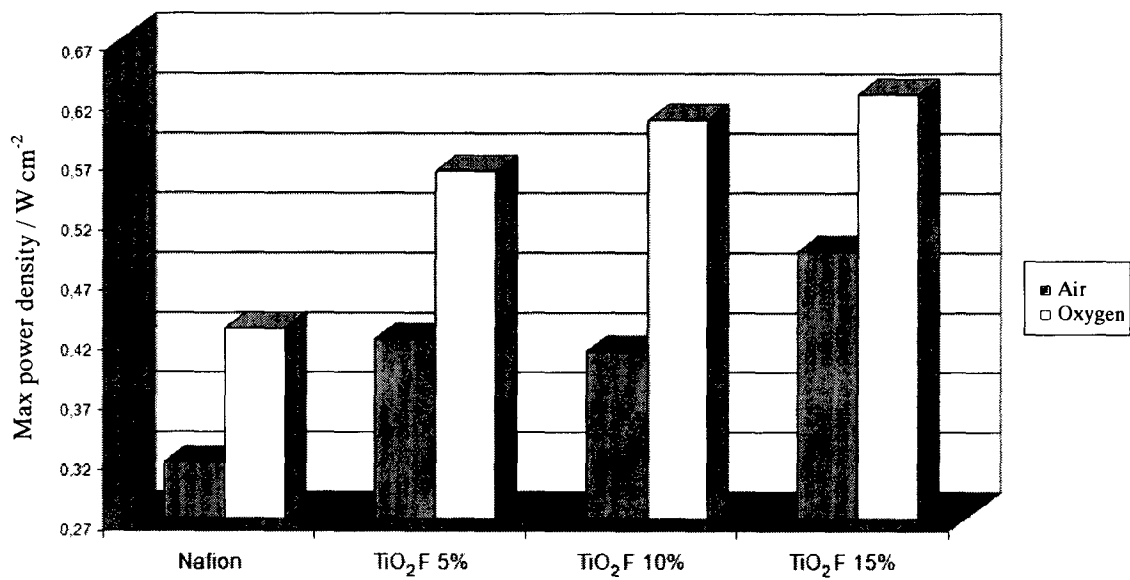


Figura 10

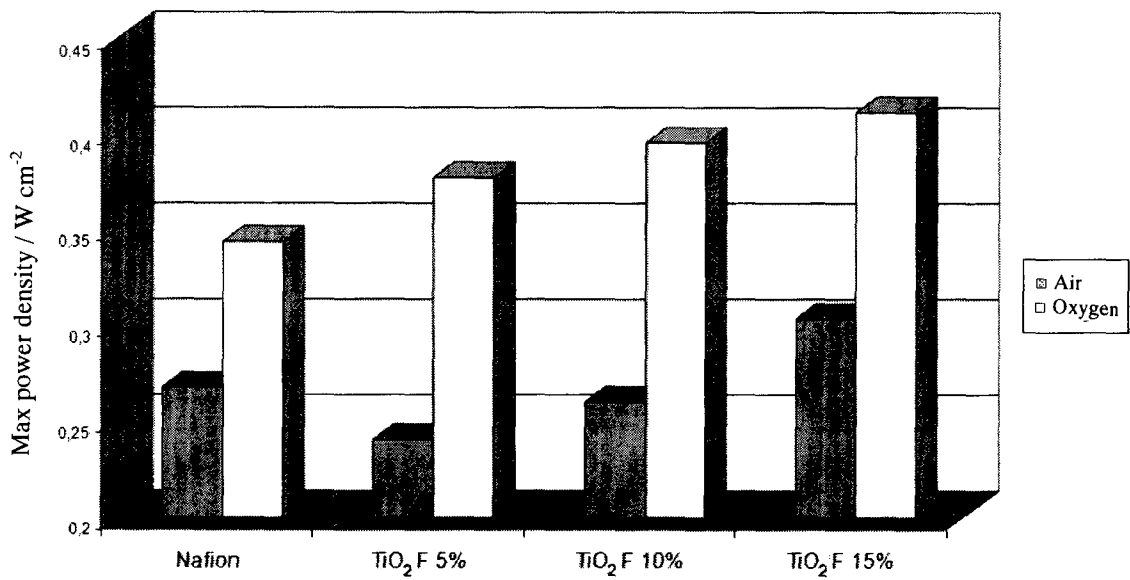


Figure 11

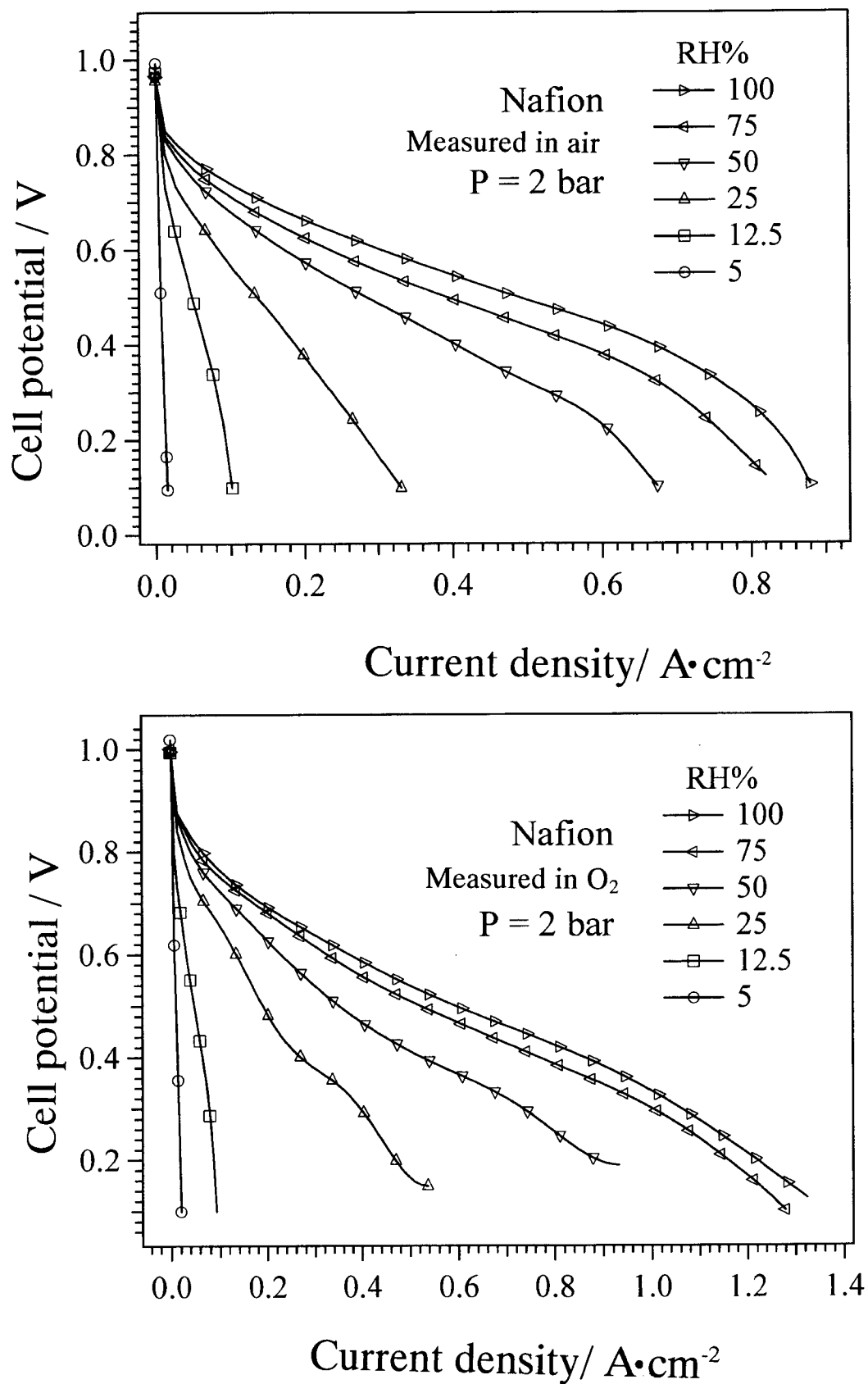


Figure 12

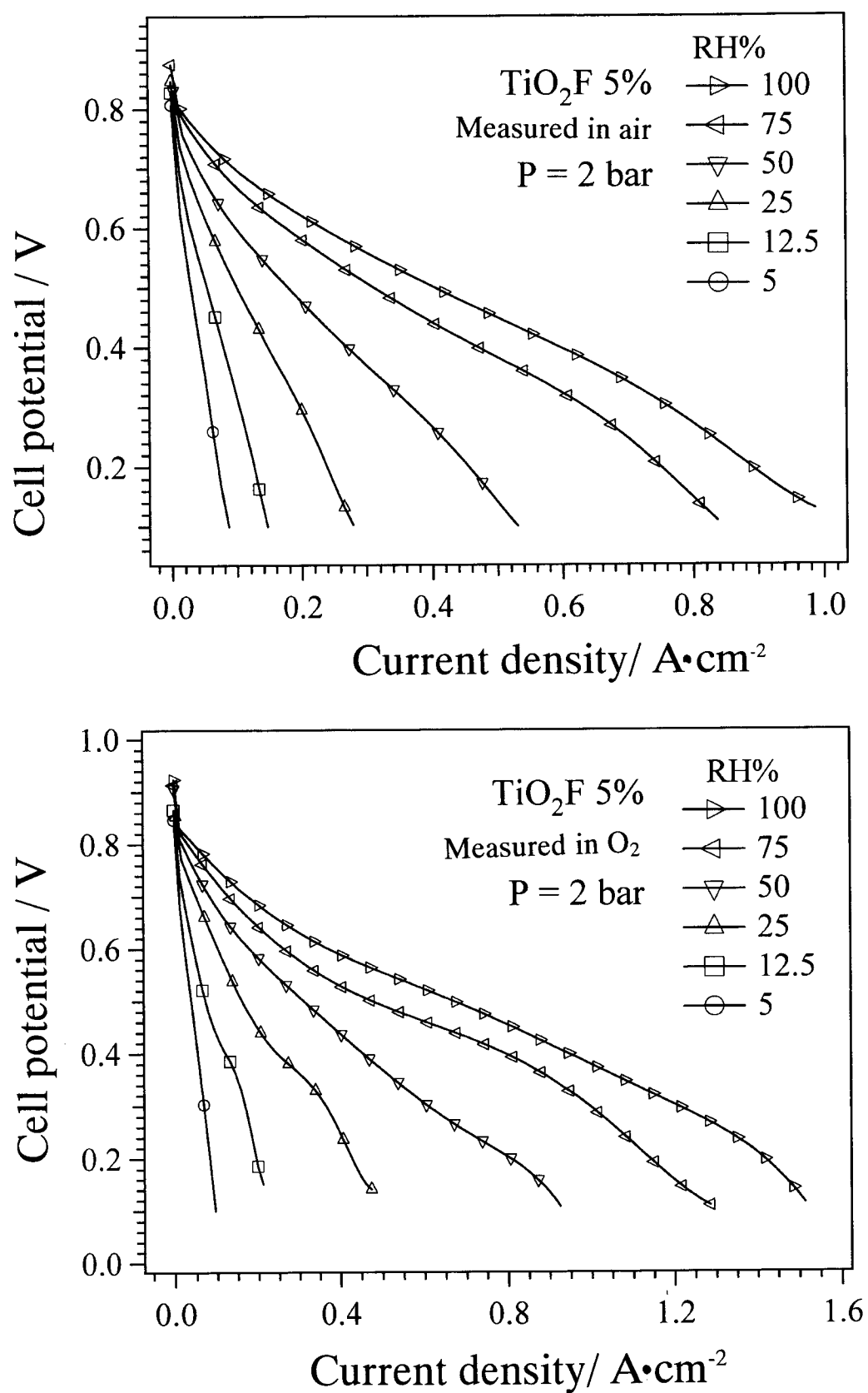


Figure 13

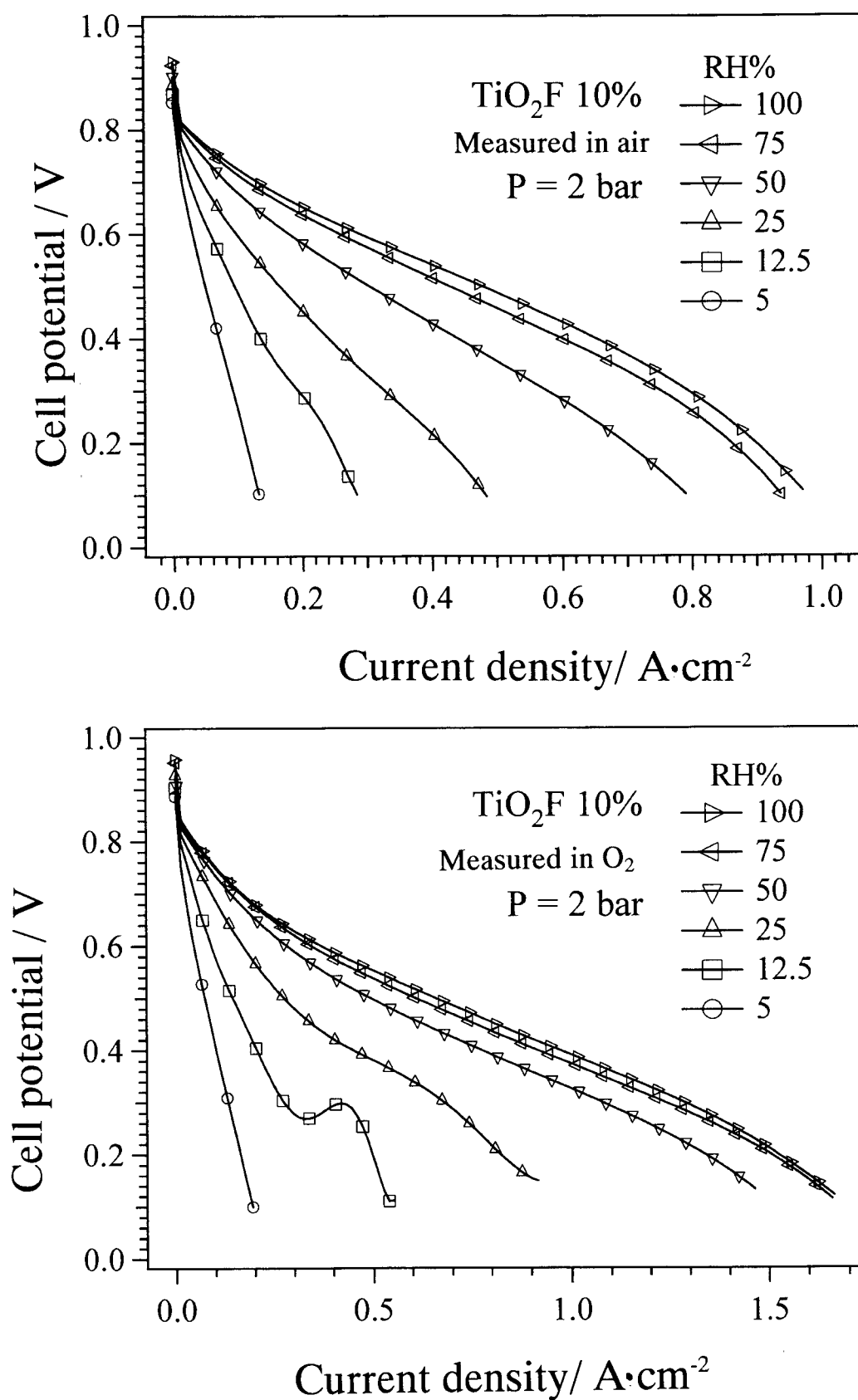


Figure 14

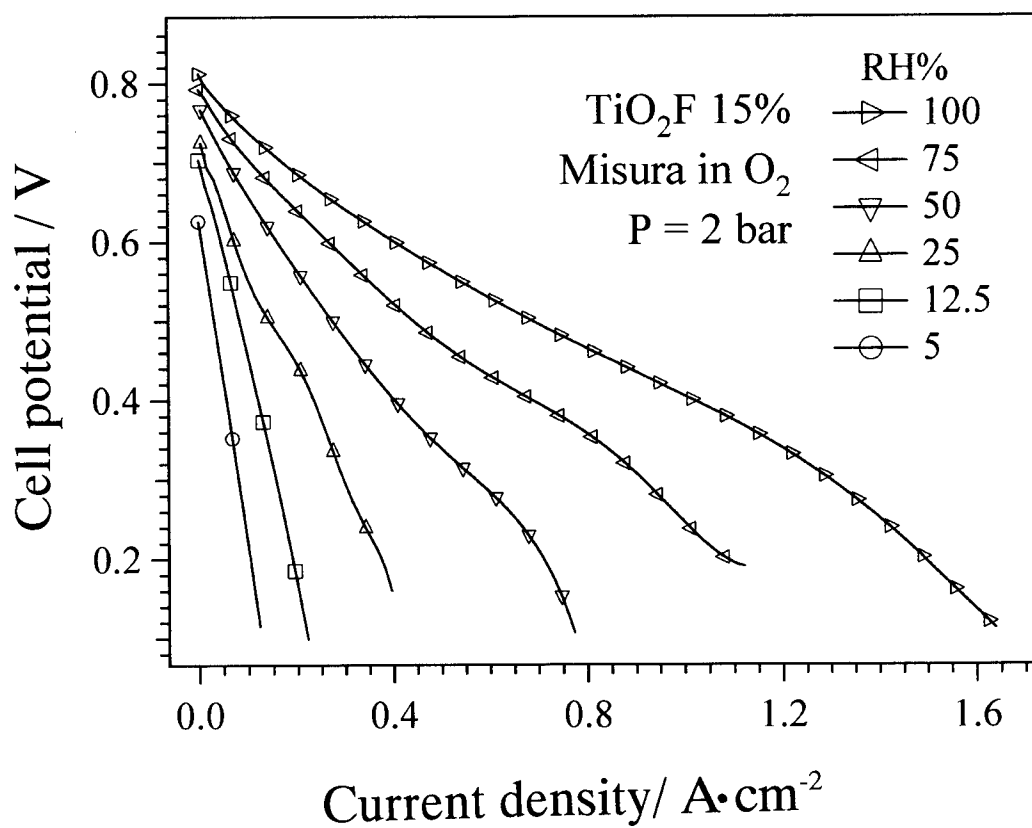
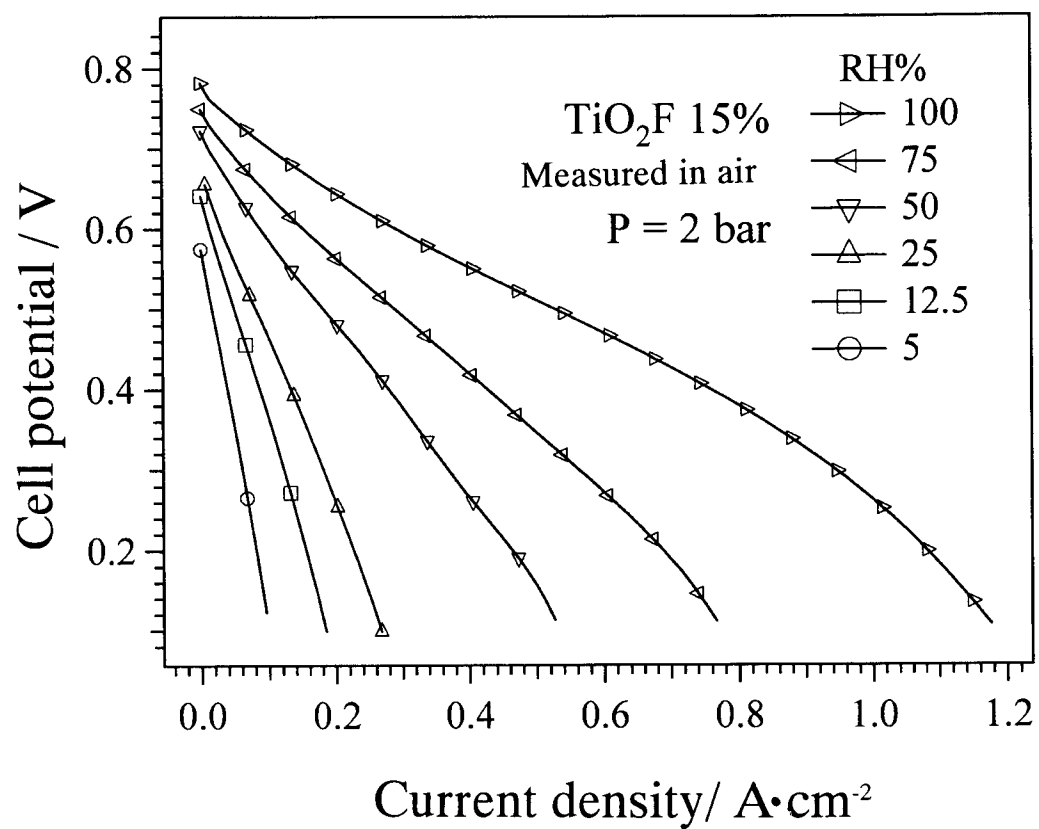
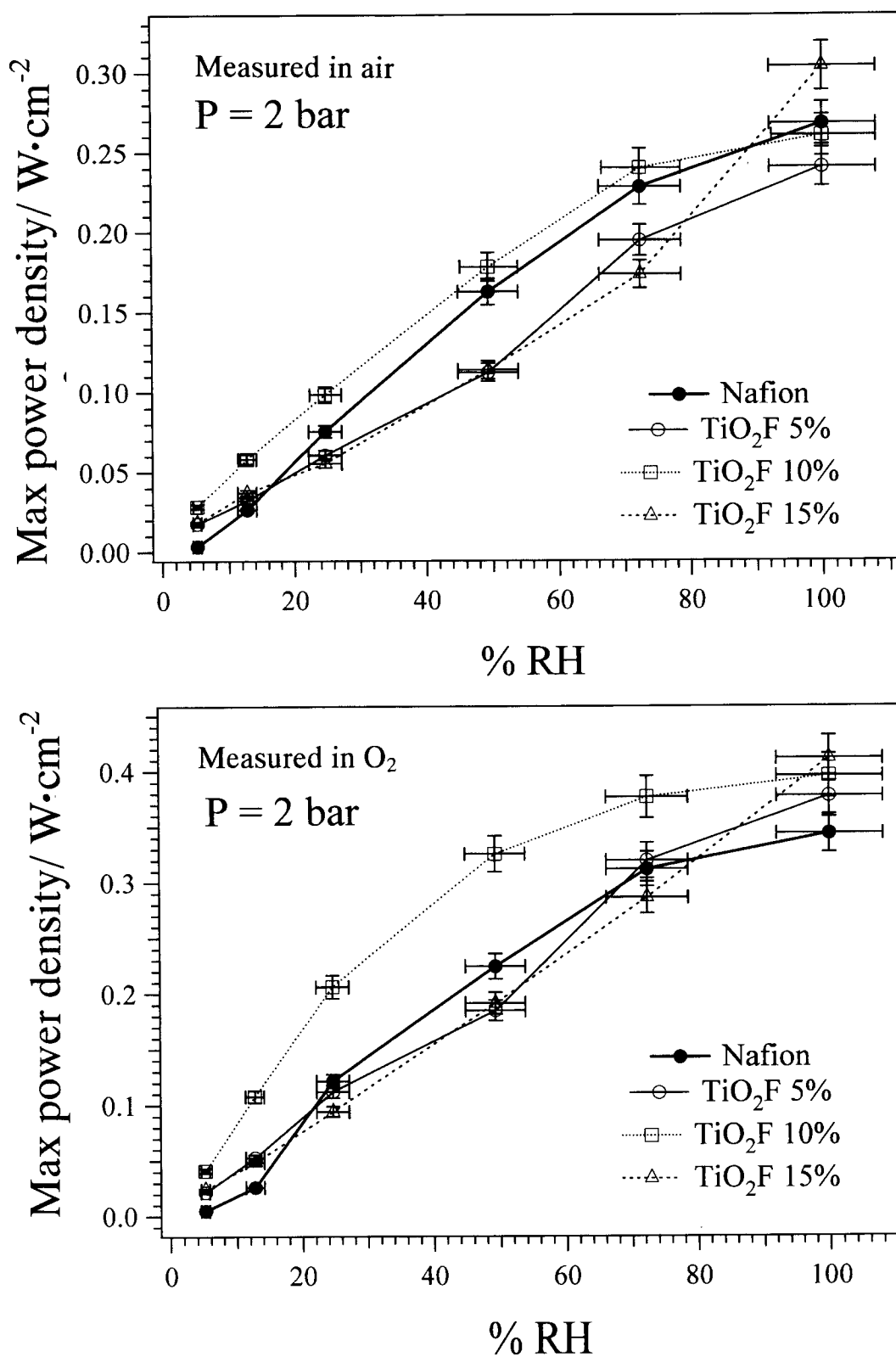


Figure 15



INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2011/053260

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01G23/047 H01M4/90 C01G23/053
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)

C01G 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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	"Results and discussion"figure 1; table 1 ----- -/--	3-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 October 2011

Date of mailing of the international search report

24/10/2011

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

Corrias, M

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2011/053260

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2006/077203 A1 (BRETON SPA [IT]; GORDIENKO PAVEL S [RU]) 27 July 2006 (2006-07-27) page 4, line 1 - page 10, line 12; claims 1-17 -----	9-22
A	TODOROVA N ET AL: "Structure tailoring of fluorine-doped TiO₂ nanostructured powders", MATERIALS SCIENCE AND ENGINEERING B, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 152, no. 1-3, 25 August 2008 (2008-08-25), pages 50-54, XP025609278, ISSN: 0921-5107, DOI: DOI:10.1016/J.MSEB.2008.06.019 [retrieved on 2008-07-09] "Experimental", "Results and discussion" -----	1-8
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Information on patent family members

International application No

PCT/IB2011/053260

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