

METHOD FOR PRODUCING A POROUS, CARBON-BASED MATERIAL

The present invention relates to a method for producing a porous, carbon-based material by pyrolysis and/or carbonization of polymer films selected from films or lacquers in an atmosphere that is essentially free of oxygen at temperatures in the range of 80 °C to 3,500 °C.

Porous, carbon-based materials have been used in the area of fluid separation for quite some time. Such materials may be prepared and used in suitable form as adsorbents, membrane layers, or self-supporting membranes. The various possibilities to specifically change both the porosity and the chemical properties of carbon-based materials make these materials especially interesting in particular for selective fluid separation tasks.

A series of methods for the preparation of porous carbon-based materials that are in two-dimensional form, in particular in sheet form, are described in the prior art. In WO 02/32558 for example is described a method for the preparation of flexible and porous adsorbents on the basis of carbon comprising materials, wherein a two-dimensional base matrix, the components of which are essentially held together by hydrogen bonds, is prepared on a paper machine and subsequently pyrolyzed. The starting materials used in this International Application are essentially fibrous substances of various kinds, since these are usually used on paper machines and the individual fibers in the prepared paper are then essentially held together by hydrogen bonds.

Similar methods are described for example in the Japanese Patent Application JP 5194056 A, as well as in the Japanese Patent Application JP 61012918. In these documents, papermaking processes are also described, with the help of which sheets of paper are manufactured from organic fibers or plastic fibers as well as pulp that are treated with



phenol resin and subsequently dried, hot pressed, and carbonated in an inert gas atmosphere. In this manner, thick, porous carbon sheets with resistance against chemicals and electrical conductivity may be obtained.

However, a disadvantage of the methods described above is that the fiber materials used in the starting material largely predetermine, depending upon their fiber thickness and fiber length as well as their distribution in the sheet-like paper material, the density and therewith also the porosity of the resulting carbon material after pyrolysis, so that with pores with oversized dimensions additional complex aftertreatment steps such as chemical vapor phase infiltration are necessary in order to narrow the pores by deposition of additional carbon material.

Furthermore, according to the methods of the prior art only starting materials that are usable in a necessarily aqueous paper processing process may be used which severely limits the selection of the possible starting materials, particularly in the area of hydrophobic plastics. Just such hydrophobic plastics, such as for example polyolefins, are, however, often preferred starting materials over natural fibers due to their relatively high carbon content and the easy availability in constant quality.

Therefore, there is a need for a cost-effective and simple method for the preparation of porous carbon-based materials that does without the necessity of the use of paper-like materials prepared from fibers.

It is therefore the object of the present invention to provide a method for the preparation of porous, essentially carbon-based materials that allows for the preparation of the respective materials from starting materials that are cheap and with respect to their properties widely variable in a cost effective manner and with few process steps.

A further object of the present invention is the provision of a method for the preparation of porous carbon-based materials that allows for the preparation of stable self-supporting structures or membranes or membrane layers from porous carbon-based material.

The solution according to the invention of the objects stated above consists in a method for the preparation of porous, carbon-based material that comprises the following steps:

- a) provision of a polymer film selected from films or coatings
- b) pyrolysis and/or carbonization of the polymer film in an atmosphere that is essentially free of oxygen at temperatures in the range of 80 °C to 3,500 °C.

In preferred embodiments of the present invention, the pyrolysis and/or carbonization of the polymer film is carried out in an atmosphere that is essentially free of oxygen at temperatures in the range of 200 °C to 2,500 °C.

According to the invention, it was found that from polymer films that comprise both films of suitable polymer materials and coatings, carbon materials may be made by pyrolysis and/or carbonization at high temperatures, the porosity of which may be specifically adjusted in wide ranges depending upon the polymer film material that was used, its thickness and structure.

Polymer films have the advantage that they are easily prepared or commercially available in almost any dimension. Polymer films are easily available and cost-effective. In contrast to paper as starting material for the pyrolysis and/or carbonization, polymer films, particularly films and

coatings such as for example lacquers, have the advantage that hydrophobic materials that usually may not be used with the pulps or water-compatible natural fibers used in papermaking, may be used for the preparation of carbon-based materials.

Polymer film are easily formable and may for example be processed to larger ensembles and structures prior to pyrolysis or carbonization, such structures essentially being maintained during pyrolysis/carbonization of the polymer film material. In this manner, it is possible by multiple layering on top of each other of polymer films to film or sheet packages and subsequent pyrolysis and/or carbonization according to the method of the present invention to generate package or modular structures from porous carbon-based material that due to the mechanical strength of the resulting material may be used as self-supporting, mechanically stable membrane or adsorber packages in fluid separation.

Prior to pyrolysis and/or carbonization, the polymer films may be structured in a suitable manner by folding, stamping, die-cutting, printing, extruding, spraying, injection molding, gathering and the like, and may optionally be bonded to one another. For this, conventional known adhesives and other suitable adhesive materials such as for example water glass, starch, acrylates, cyanoacrylates, hot melt adhesives, rubber, or solvent-containing as well as solvent-free adhesives, etc. may be used, whereby the method according to the invention allows for the preparation of specifically constructed three-dimensional structures with ordered build-up from the desired porous carbon-based material.

In this connection, the carbon-based material does not have to be prepared first and then, afterwards, in complex forming steps, the desired three-dimensional structure that

is required for example for membrane packages, etc. is prepared, but the method according to the invention allows for the giving of the finished structure of the carbon-based material by suitable structuring or forming of the polymer film already prior to the pyrolysis and/or carbonization.

Consequently, by the method according to the invention, difficult small-spaced structures may also be created that cannot or only with difficulty be accomplished from finished carbon material by means of subsequent forming. In this connection, for example the shrinkage usually occurring during pyrolysis and/or carbonization may be specifically used.

The polymer films that are usable according to the invention may be provided two-dimensionally in sheet or web form, e.g. as rolls of material, or also in tube form or in a tubular or capillary geometry. Polymer films in form of films or capillaries may be prepared for example by means of phase inversion methods (asymmetrical layer build-up) from polymer emulsions or suspensions.

Suitable polymer films in the method of the present invention are for example films, tubes, or capillaries from plastics. Preferred plastics comprise homo- or copolymers of aliphatic or aromatic polyolefins, such as polyethylene, polypropylene, polybutene, polyisobutene, polypentene; polybutadiene; polyvinyls such as polyvinyl chloride or polyvinyl alcohol, poly(meth)acrylic acid, polyacrylonitrile, polyacryloylcyanoacrylate; polyamide; polyester, polyurethane, polystyrene, polytetrafluoroethylene; polymers such as collagen, albumin, gelatin, hyaluronic acid, starch, celluloses such as methylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose phthalate; waxes, paraffin waxes, Fischer-Tropsch-waxes;

casein, dextrans, polysaccharides, fibrinogen, poly(D,L-lactides), poly(D,L-lactides-co-glycolides), polyglycolides, polyhydroxybutylates, polyalkylcarbonates, polyorthoesters, polyhydroxyvaleric acid, polydioxanones, polyethylene terephthalate, polymalatic acid, polytartronic acid, polyanhydrides, polyphosphazenes, polyaminoacids; polyethylene vinylacetate, silicones; poly(ester-urethanes), poly(ether-urethanes), poly(ester-ureas), polyethers such as polyethylene oxide, polypropylene oxide, pluronics, polytetramethylene glycol; polyvinyl pyrrolidone, poly(vinyl acetate phthalate), mixtures of homo- or copolymers of one or more of the aforementioned materials as well as additional polymer materials known to those skilled in the art that may also be typically processed to films, tubes or capillaries.

Other preferred kinds of polymer films are polymer foam systems, for example phenol foams, polyolefin foams, polystyrene foams, polyurethane foams, fluoropolymer foams that may be converted into porous carbon materials in a subsequent carbonization or pyrolysis step according to the invention. These have the advantage that in the carbonization step, materials with a pore structure that is adjustable depending upon the foam porosity may be achieved. For the preparation of the foamed polymers, all conventional foaming methods of the state of the art using conventional blowing agents such as halogenated hydrocarbons, carbon dioxide, nitrogen, hydrogen and low-boiling hydrocarbons may be used. Fillers may also be applied into or onto the polymer films that are suitable to cause foam formation in or on the polymer film.

Furthermore, in the method according to the invention, the polymer film may be a coating, such as for example a lacquer film, that was produced from a lacquer with a binder base of alkyd resin, chlorinated rubber, epoxy resin, formaldehyde resin, (meth)acrylate resin, phenol

resin, alkylphenol resin, amine resin, melamine resin, oil base, nitro base (cellulose nitrate), polyester, polyurethane, colophony, Novolac[®] - epoxy resins, vinylester resin, tar or tar-like substances such as tar pitch, bitumen, as well as starch, cellulose, shellac, waxes, modified binders of the aforementioned substances, or binders of organic renewable raw materials, or combinations of the mentioned substances.

Especially preferred are lacquers on the basis of phenol and/or melamine resins that may optionally be fully or partially epoxidized, e.g. commercial packing lacquers such as one- or two-component lacquers on the basis of optionally epoxidized aromatic hydrocarbon resins.

Coatings that may be used according to the invention may be applied to a suitable carrier material from the liquid, pulpy, or paste-like state e.g. by coating, painting, lacquering, phase inversion, atomizing, dispersion or hot-melt coating, extruding, casting, dipping, or as hot melts from the solid state by means of powder coating, flame spraying, sintering or the like according to known methods. The lamination of carrier materials with suitable polymers is also a method that is usable according to the invention for the provision of the polymer film in form of a coating.

The use of coatings in the method according to the invention may for example occur in such a way that a coating is applied to an inert carrier material, optionally dried, and subsequently subjected to pyrolysis and/or carbonization, the carrier material being essentially completely pyrolyzed or carbonized through suitable selection of the pyrolysis or carbonization conditions, so that the coating such as for example a lacquer remains after pyrolysis or carbonization in form of a porous carbon-based material. In the method according to the invention, the use of coatings, particularly of lacquers,

finishes, laminates and the like allows for the preparation of especially thin carbon-based materials in sheet form.

Furthermore, preferred polymer films may also be obtained by transfer methods, wherein materials, lacquers, finishes, laminates of the aforementioned materials or polymer materials are applied to transfer carrier material such as for example films as mentioned above, are optionally cured, and afterwards stripped from the carrier material in order to subsequently be supplied to the carbonization.

In this connection, the coating of the carrier material may occur by suitable printing methods such as e.g. anilox-roller printing, knife coating, spray coating, or thermal, pressed, or wet-on-wet laminations and the like. Several thin layers are possible and optionally desired in order to guarantee e.g. accuracy of the polymer film. Furthermore, during the application of the coatings onto the transfer carrier material, different gratings may optionally be used for a lacquer distribution that is as homogeneous as possible.

With transfer methods of the kind described above it is also possible to produce multilayer graded films with different layer material sequences that after carbonization give carbon-based graded materials wherein for example the density of the material may vary depending upon the location.

In case very thin polymer films are required for use in the method according to the invention, these may be produced on suitable films by the transfer method through e.g. powder coating or hot-melt coating and then stripped and carbonized. In case the carrier film is to be completely volatilized under carbonization conditions, such as e.g. polyolefin films, a stripping from the carrier film may not be necessary or even preferred.

Furthermore, by the transfer method it is also possible to achieve a structuring or microstructuring of the produced polymer films by appropriately pre-structuring the transfer carrier material, e.g. through prior plasma etching. With thin coating, the structure of the carrier material is transferred to the polymer film in this way.

In certain embodiments of the invention, the polymer film may also be applied as coating to temperature-resistant substrates in order to give, after pyrolysis or carbonization, carbon-based, porous layers for use as membrane or molecular layer. The substrates may consist of e.g. glass, ceramics, metal, metal alloys, metal oxides, silicon oxides, aluminum oxides, zeolite, titanium oxide, zirconium oxide, as well as mixtures of these materials and may be pre-formed as desired. A preferred use of this embodiment is the preparation of adsorber pellets with membrane coating from the material producible according to the invention.

The polymer film used in the method of the present invention may in certain preferred embodiments be coated, impregnated, or modified with organic and/or inorganic compounds prior to pyrolysis and/or carbonization. A coating applied to one or both sides of the polymer film may for example comprise: epoxy resins, phenol resin, tar, tar pitch, bitumen, rubber, polychloroprene or poly(styrene-co-butadiene) latex materials, siloxanes, silicates, metal salts or metal salt solutions, for example transition metal salts, carbon black, fullerenes, active carbon powder, carbon molecular sieve, perovskite, aluminum oxides, silicon oxides, silicon carbide, boron nitride, silicon nitride, precious metal powder such as for example Pt, Pd, Au, or Ag; as well as combinations thereof.

Preferred modifications may be obtained for example by superficial parylenization or impregnation of the polymer films or the carbon-based materials obtained therefrom. In this connection, at first, the polymer films are treated at higher temperature, typically about 600 °C, with paracyclophane, a layer of poly(p-xylylene) being formed superficially on the polymer films or materials created therefrom. This may optionally be converted into carbon in a succeeding carbonization or pyrolysis step.

In especially preferred embodiments, the step sequence of parylenization and carbonization is repeated several times.

Through one- or two-sided coating of the polymer film with the materials mentioned above or also through specific incorporation of such materials in the polymer film structure, the properties of the porous carbon-based material resulting after pyrolysis and/or carbonization may be specifically influenced and improved. For example through incorporation of layered silicates into the polymer film or coating of the polymer film with layered silicates, nanoparticles, inorganic nanocomposite metals, metal oxides and the like, the thermal expansion coefficient of the resulting carbon material as well as its mechanical properties or porosity properties may be modified.

In particular during the preparation of coated substrates that are provided with a layer of the material prepared according to the invention, through the incorporation of the aforementioned additives into the polymer film there is the possibility to improve the adherence of the applied layer to the substrate and for example to adjust the thermal expansion coefficient of the outer layer to the one of the substrate so that these coated substrates become more resistant to breaks in and flaking of the membrane layer. Consequently, these materials are substantially more

durable and have a higher long-term stability in concrete use as conventional products of this kind.

The application or the incorporation of metals and metal salts, in particular also of precious metals and transition metals, allows for the adjustment of the chemical and adsorptive properties of the resulting porous carbon-based material to each of the desired requirements so that for special applications, the resulting material may also be provided with for example heterogeneous catalytic properties.

In preferred embodiments of the method according to the invention, the physical and chemical properties of the porous carbon-based material are further modified after pyrolysis or carbonization through appropriate aftertreatment steps and are adjusted to each of the desired applications.

Suitable aftertreatments are for example reducing or oxidative aftertreatment steps, wherein the material is treated with suitable reducing agents and/or oxidizing agents such as hydrogen, carbon dioxide, water vapor, oxygen, air, nitric acid and the like, as well as optionally mixtures thereof.

The aftertreatment steps may optionally be carried out at a higher temperature, but below the pyrolysis temperature, for example from 40 °C to 1,000 °C, preferably 70 °C to 900 °C, more preferably 100 °C to 850 °C, even more preferably 200 °C to 800 °C, and most preferably 700 °C. In especially preferred embodiments, the material prepared according to the invention is modified reductively or oxidatively, or with a combination of these aftertreatment steps at room temperature.

Through oxidative or reductive treatment or also through the incorporation of additives, fillers, or functional

materials, the surface properties of the materials prepared according to the invention may be specifically influenced or changed. For example, through incorporation of inorganic nanoparticles or nanocomposites such as layered silicates, the surface properties of the material may be hydrophilized or hydrophobized.

Additional suitable additives, fillers, or functional materials are for example silicon or aluminum oxides, aluminosilicates, zirconium oxides, talcum, graphite, carbon black, zeolites, clay materials, phyllosilicates and the like that are typically known to those skilled in the art.

In preferred embodiments, the adjustment of the porosity may occur through washing out of fillers such as for example polyvinylpyrrolidone, polyethylene glycol, aluminum powder, fatty acids, microwaxes or emulsions, paraffins, carbonates, dissolved gases, or water-soluble salts with water, solvent, acids or bases, or by distillation or oxidative or non-oxidative decomposition. The porosity may optionally also be generated by structuring of the surface with powdery substances such as for example metal powder, carbon black, phenol resin powder, fibers, in particular carbon or natural fibers.

The addition of aluminum-based fillers for example results in an increase of the thermal expansion coefficient, and addition of glass, graphite, or quartz-based fillers results in a decrease of the thermal expansion coefficient, so that by mixing of the components in the polymer system the thermal expansion coefficient of the materials according to the invention may accordingly be adjusted individually. A further possible adjustment of the properties may for example, and not exclusively, occur through preparation of a fiber composite by means of addition of carbon, polymer, glass, or other fibers in

woven or nonwoven form, which results in a noticeable increase of the elasticity and other mechanical properties of the coating.

The materials prepared according to the invention may also later be provided with biocompatible surfaces by incorporation of suitable additives and optionally be used as bioreactors or excipients. For this, for example drugs or enzymes may be introduced in the material, the former being optionally controllably released through suitable retarding and/or selective permeation properties of the membranes.

Furthermore, it is preferred in certain embodiments to fluorinate the materials prepared according to the invention. Depending upon the degree of fluorination applied, the materials according to the invention may be provided with lipophobic properties with a high degree of fluorination, and with lipophilic properties with a low degree of fluorination.

Moreover, it is optionally preferred to at least superficially hydrophilize the materials according to the invention by treatment with water-soluble substances such as for example polyvinylpyrrolidone or polyethylene glycols, polypropylene glycols.

Through these measures, the wetting behavior of the materials may be modified in the desired manner.

The carbonized material may also optionally be subjected to a so-called CVD process (Chemical Vapor Deposition) in an additional optional process step in order to further modify the surfaces or pore structure and their properties. For this, the carbonized material is treated with suitable precursor gases at high temperatures. Such methods have been known for a long time in the state of the art.

Almost all known saturated and unsaturated hydrocarbons with sufficient volatility under CVD-conditions are considered as carbon-cleaving precursors. Examples are methane, ethane, ethylene, acetylene, linear and branched alkanes, alkenes, and alkynes with carbon numbers of $C_1 - C_{20}$, aromatic hydrocarbons such as benzene, naphthalene, etc., as well as singly and multiply alkyl, alkenyl, and alkynyl-substituted aromatics such as for example toluene, xylene, cresol, styrene, etc.

BCl_3 , NH_3 , silanes such as tetraethoxysilane (TEOS), SiH_4 , dichlorodimethylsilane (DDS), methyltrichlorosilane (MTS), trichlorosilyldichloroborane (TDADB), hexadichloromethylsilyl oxide (HDMSO), $AlCl_3$, $TiCl_3$ or mixtures thereof may be used as ceramics precursors.

These precursors are mostly used in CVD-methods in small concentrations of about 0.5 to 15 percent by volume with an inert gas, such as for example nitrogen, argon or the like. The addition of hydrogen to appropriate depositing gas mixtures is also possible. At temperatures between 200 and 2,000 °C, preferably 500 to 1,500 °C, and most preferably 700 to 1,300 °C, the mentioned compounds cleave hydrocarbon fragments or carbon or ceramic precursors that deposit essentially uniformly distributed in the pore system of the pyrolyzed material, modify the pore structure there, and that way cause an essentially homogeneous pore size and pore distribution in the sense of a further optimization.

For the control of the uniform distribution of the deposited carbon or ceramic particles in the pore system of the carbonized material, for example during the deposition of the carbon precursors on a surface of the carbonized object, a pressure gradient, e.g. in form of a continuous negative pressure or vacuum, may be applied, whereby the deposited particles are uniformly sucked into the pore

structure of the carbonized substance (so-called „forced flow CVI“, Chemical Vapor Infiltration; see e.g. W. Benzinger et. al., Carbon 1996, 34, page 1465). Furthermore, the homogenization of the pore structure achieved in this manner increases the mechanical strength of the materials prepared in this manner.

This method may, in an analogous fashion, also be used with ceramic, sintered metal, metal or metal alloy precursors as mentioned above.

Furthermore, by means of ion implantation, the surface properties of the material according to the invention may be modified. Through implantation of nitrogen, nitride, carbonitride, or oxynitride phases with included transition metals may be formed, which noticeably increases the chemical resistance and mechanical resistivity of the carbon-containing materials. The ion implantation of carbon may be used for the increase of the mechanical strength of the materials according to the invention as well as for redensification of porous materials.

In further preferred embodiments, the material prepared according to the invention is mechanically reduced to small pieces after pyrolysis and/or carbonization by means of suitable methods, for example through milling in ball or roller mills and the like. The material prepared in this manner that was reduced to small pieces may be used as powder, flakes, rods, spheres, hollow spheres of different granulation, or may be processed to granulates or extrudates of various form by means of conventional methods of the state of the art. Hot-press methods, optionally with addition of suitable binders, may also be used in order to form the material according to the convention. All polymers that intrinsically possess membrane properties or are appropriately prepared in order to incorporate the

materials mentioned above are particularly suitable for this.

In addition, small-sized powder material may also be prepared in accordance with the method according to the invention by reducing the polymer film to small pieces in a suitable manner prior to pyrolysis and/or carbonization.

In the embodiments of the method of the present invention that are especially preferred, however, the polymer films are suitably structured prior to pyrolysis and/or carbonization, for example stamped, combined with one another to structural units, adhesively bonded, or mechanically bonded to one another, since hereby the possibility arises to suitably pre-structure polymer film material that is easily formed in a simple manner, the structure essentially remaining unchanged during the pyrolysis step.

The pyrolysis or carbonization step of the method according to the invention is typically carried out at temperatures in the range of 80 °C to 3,500 °C, preferably at about 200 °C to about 2,500 °C, most preferably at about 200 °C to about 1,200 °C. Preferred temperatures in some embodiments are at 250 °C to 500 °C. The temperature, depending on the properties of the materials used, is preferably chosen in such a way that the polymer film is essentially completely transformed into carbon-containing solid with a temperature expenditure that is as low as possible. Through suitable selection or control of the pyrolysis temperature, the porosity, the strength and the stiffness of the material, and other properties may be adjusted.

The atmosphere during the pyrolysis or carbonization step is in the method according to the invention essentially free of oxygen. The use of inert gas atmospheres, for

example of nitrogen, noble gas such as argon, neon, as well as all other inert, with carbon non-reactive gases or gaseous compounds, reactive gases such as carbon dioxide, hydrochloric acid, ammonia, hydrogen, and mixtures of inert gases, is preferred. Nitrogen and/or argon are preferred. In some cases, after carbonization activation with the reactive cases, which then also comprise oxygen or water vapor, may occur in order to achieve the desired properties.

The pyrolysis and/or carbonization in the method according to the invention is typically carried out at normal pressure in the presence of inert gases as mentioned above. Optionally, however, the use of higher inert gas pressures may also be advantageous. In certain embodiments of the method according to the invention, the pyrolysis and/or carbonization may also occur at negative pressure or in vacuo.

The pyrolysis step is preferably carried out in a continuous furnace process. Thereby, the optionally structured, coated, or pretreated polymer films are supplied to the furnace on one side and exit the furnace at the other end. In preferred embodiments, the polymer film or the object formed from polymer films may lie on a perforated plate, a screen or the like so that negative pressure may be applied through the polymer film during pyrolysis and/or carbonization. This not only allows for a simple fixation of the objects in the furnace but also for exhaustion and optimal flowing of the inert gas through the films or structural units during pyrolysis and/or carbonization.

By means of appropriate inert gas locks, the furnace may be subdivided into individual segments, wherein successively one or more pyrolysis or carbonization steps may be carried out, optionally under different pyrolysis or carbonization

conditions, such as for example different temperature levels, different inert gases or vacuum.

Furthermore, in appropriate segments of the furnace, aftertreatment steps such as reactivation through reduction or oxidation or impregnation with metals, metal salt solutions, or catalysts, etc. may also optionally be carried out.

Alternatively to this, the pyrolysis/carbonization may also be carried out in a closed furnace, which is in particular then preferred, when the pyrolysis and/or carbonization is to be carried out in vacuo.

During pyrolysis and/or carbonization in the method according to the invention, a decrease in weight of the polymer film of about 5 % to 95 %, preferably about 40 % to 90 %, most preferably 50 % to 70 %, depending upon the starting material and pre-treatment used, typically occurs. Moreover, during pyrolysis and/or carbonization in the method according to the invention, shrinkage of the polymer film or of the structure or structural unit created from polymer films normally occurs. The shrinkage may have a magnitude of 0 % to about 95 %, preferably 10 % to 30 %.

The materials prepared according to the invention are chemically stable, mechanically loadable, electrically conductive, and heat resistant.

In the method according to the invention, the electrical conductivity may be adjusted, depending upon the pyrolysis or carbonization temperature used and the nature and amount of the additive or filler employed, in wide ranges. Thus, with temperatures in the range of 1,000 to 3,500 °C, due to the occurring graphitization of the material, a higher conductivity may be achieved than with lower temperatures. In addition, the electrical conductivity may also be

increased for example by addition of graphite to the polymer film, which then may be pyrolyzed or carbonized at lower temperatures.

The materials prepared according to the invention exhibit upon heating in an inert atmosphere from 20 °C to 600 °C and subsequent cooling to 20 °C a dimensional change of no more than +/- 10 %, preferably no more than +/- 1 %, most preferably no more than +/- 0.3 %.

The porous carbon-based material prepared according to the invention exhibits, depending upon the starting material, amount and nature of the fillers, a carbon content of at least 1 percent by weight, preferably at least 25 percent by weight, optionally also at least 60 percent by weight and most preferably at least 75 percent by weight. Material that is especially preferred according to the invention has a carbon content of at least 50 percent by weight.

The specific surface according to BET of materials prepared according to the invention is typically very small since the porosity is smaller than is detectable with this method. However, by means of appropriate additives or methods (porosity agent or activation), BET surfaces of over 2,000 m²/g are achievable.

The material prepared in accordance with the method according to the invention in sheet or powder form may be used for the preparation of membranes, adsorbents, and/or membrane modules or membrane packages. The preparation of membrane modules in accordance with the method according to the invention may for example occur as described in WO 02/32558, a polymer film being used instead of the paper base matrix described therein. The disclosures of WO 02/32558 are incorporated herein by reference.

Examples for the use of the material prepared according to the invention in the area of fluid separation are: general gas separation such as for example oxygen-nitrogen separation for the accumulation of oxygen from air, separation of hydrocarbon mixtures, isolation of hydrogens from hydrogen-containing gas mixtures, gas filtration, isolation of CO₂ from ambient air, isolation of volatile organic compounds from exhaust gases or ambient air, purification, desalting, softening or recovery of drinking water, as fuel cell electrode, in form of Sulzer packages, Raschig rings and the like.

In a special embodiment of the present invention, the polymer film is applied to conventional adsorber materials or membranes such as activated carbon, zeolite, ceramics, sintered metals, papers, wovens, nonwovens, metals, or metal alloys and the like, preferably to adsorber materials in form of pellets or granulate, for example in form of a surface coating, prior to pyrolysis or carbonization.

After pyrolysis or carbonization, adsorber materials with a superficial membrane layer may be prepared that may, whereby the selectivity of the adsorbers is determined by the selectivity of the membrane. In this manner, for example adsorber granulates may be prepared that selectively adsorb only those substances that are able to permeate through the membrane. A quick exhaustion of the adsorber due to covering with undesirable accessory components is thereby protracted or avoided. Hereby, the exchange intervals of adsorber cartridges in appropriate applications may be prolonged, which leads to an increased cost effectiveness.

Preferred applications of such membrane-coated adsorbers are for example in PSA systems, in automotive or airplane cabins, breathing protection systems such as gas masks, etc.

EXAMPLES

Example 1: Pyrolysis and carbonization of cellulose acetate film coated thinly on both sides with nitrocellulose, manufacturer UCB Films, type Cellophane[®] MS 500, total thickness 34.7 microns, 50 g/m².

The film was pyrolyzed or carbonized at 830 °C in purified nitrogen atmosphere (flow rate of 10 liter/min.) over a period of time of 48 hours in a commercial high-temperature furnace. Subsequently, the shrinkage occurring thereby was determined by comparison of the averaged measured values of each of three rectangular film pieces and the carbon sheets prepared therefrom. The results are compiled in Table 1.

Table 1: Shrinkage of the nitrocellulose-coated film

Cellophane [®] MS 500	Prior to pyrolysis	After pyrolysis	difference [%]
Length a [mm]	120	70	41.7
Length b [mm]	60	44	26.7
Area [mm ²]	7,200	3,080	57.2
Weight [g]	0.369	0.075	79.7

Subsequently, the nitrogen and hydrogen permeability of the carbon sheets prepared above was tested under different conditions. The conditions and results are listed below in Table 2. The permeability values are average values from three measurements each.

Table 2: Membrane data:

Gas	Temperature [°C]	Pressure [bar]	Time [sec]	Membrane area [m ²]	Permeability [l/m ² *h*bar]
N ₂	25	0.10	Not measurable	0.000798	-
N ₂	25	0.20	Not measurable	0.000798	-
N ₂	25	0.50	Not measurable	0.000798	-

N ₂	25	1.00	Not measurable	0.000798	-
H ₂	25	0.20	69.0	0.000798	33
H ₂	25	0.30	60.0	0.000798	25
H ₂	25	0.40	58.0	0.000798	19
H ₂	25	0.50	58.0	0.000798	16
H ₂	25	0.99	39.1	0.000798	12
H ₂	25	2.00	24.9	0.000798	9
H ₂	25	2.5	Torn	0.000798	-

Example 2: Pyrolysis and carbonization of cellulose acetate films coated thinly on both sides with polyvinylidene chloride (PVdC), manufacturer UCB Films, type Cellophane[®] XS 500, total thickness 34.7 microns, 50 g/m².

The film was pyrolyzed or carbonized at 830 °C in purified nitrogen atmosphere (flow rate of 10 liter/min.) over a period of time of 48 hours in a commercial high-temperature furnace. Subsequently, the shrinkage occurring thereby was determined by comparison of the averaged measured values of each of three rectangular film pieces and the carbon sheets prepared therefrom. The results are compiled in Table 3.

Table 3: Shrinkage of the PVdC-coated film

Cellophane [®] XS 500	Prior to pyrolysis	After pyrolysis	Difference [%]
Length a [mm]	120	67	44.2
Length b [mm]	60	41	31.7
Area [mm ²]	7,200	2,747	61.9
Weight [g]	0.377	0.076	79.8

Example 3: Pyrolysis and carbonization of homogeneous and defect-free epoxy resin films, total thickness 7 microns prior to carbonization, 2.3 microns after carbonization.

The film was prepared by a solvent evaporation method from a 20 percent by weight solution.

The carbonization occurred at 830 °C in a purified nitrogen atmosphere (flow rate of 10 liter/min.) over a period of time of 48 hours in a commercial high-temperature furnace. Subsequently, the shrinkage occurring thereby was determined by comparison of the averaged measured values of each of three rectangular film pieces and the carbon sheets prepared therefrom. The results are compiled in Table 4.

Table 4: Shrinkage of the epoxy film

	Prior to pyrolysis	After pyrolysis	Difference [%]
Length a [mm]	100	46	54
Length b [mm]	100	44	56
Area [mm ²]	10,000	2,024	78
Weight [g]	0.0783	0.0235	70

The sheet material prepared in this manner was

- a) In a second activation step subjected to a second temperature treatment in air at 350 °C for 2 hours.
- b) In a second step provided with a hydrocarbon CVD layer, carried out at 700 °C in a second temperature treatment.

Thereby, the water-absorption capacity changed, which was measured as follows: 1 mL VE water was placed on the film surface with a pipette (20 mm diameter each) and allowed to act for 5 minutes. Afterwards, the weight difference was determined.

	Water absorption [g]
Carbonized sample	0,0031
<u>a) Activated sample</u>	<u>0,0072</u>

b) CVD-modified sample 0,0026.

It can be seen herefrom that the CVD modification reduces the porosity, while the activation increases the porosity of the sheet material.

Example 4: Pyrolysis and carbonization of homogeneous and defect-free epoxy resin films, total thickness 3 g/m².

The film was prepared by a solvent evaporation method from a 15 percent by weight epoxy coating solution to which was added 50 % of a polyethylene glycol (based on epoxy resin lacquer, Mw 1,000 g/mol) in a dip coating method on stainless steel substrates with a 25 mm diameter.

The carbonization occurred at 500 °C in a purified nitrogen atmosphere (flow rate of 10 liter/min.) over a period of time of 8 hours in a commercial high-temperature furnace.

Subsequently, the coating was washed out at 60 °C for 30 minutes in an ultrasound bath in water and weighed.

Weight round plate without coating:	1.2046 g
Weight after coating	1.2066 g
Weight after carbonization	1.2061 g
Weight after washing-out procedure	1.2054 g.

The porosity of the films can be increased by the washing-out procedure.

CLAIMS

1. A method for the preparation of porous carbon-based material, comprising the following steps:
 - a) provision of a polymer film selected from films or coatings;
 - b) pyrolysis and/or carbonization of the polymer film in an atmosphere that is essentially free of oxygen at temperatures in the range of 80 °C to 3,500 °C.
2. The method according to claim 1,
characterized in that the polymer film is structured prior to pyrolysis and/or carbonization by stamping, folding, die-cutting, printing, extruding, combinations thereof and the like.
3. The method according to claim 1 or claim 2,
characterized in that the polymer film comprises films of homo or copolymers of aliphatic or aromatic polyolefins such as polyethylene, polypropylene, polybutene, polyisobutene, polypentene, polybutadiene, polyvinyls such as polyvinyl chloride or polyvinyl alcohol, poly(meth)acrylic acid, polyacrylonitrile, polyamide, polyester, polyurethane, polystyrene, polytetrafluorethylene, mixtures and combinations of these homo or copolymers.
4. The method according to claim 1 or claim 2,
characterized in that the polymer film is a coating selected from lacquer, laminate, or finish.
5. The method according to claim 4,
characterized in that the polymer film is a lacquer film prepared from a lacquer with a binder base of

- alkyd resin, chlorinated rubber, epoxy resin, acrylate resin, phenol resin, amine resin, oil base, nitro base, polyester, polyurethane, phenol resin, tar, tar-like materials, tar pitch, bitumen, starch, cellulose, shellac, organic materials from renewable raw materials, or combinations thereof.
6. The method according to any of the previous claims, **characterized in that** the polymer film comprises inorganic additives or fillers.
 7. The method according to claim 6, **characterized in that** the inorganic additives or fillers are selected from silicon or aluminum oxides, aluminosilicates, zirconium oxides, talcum, graphite, carbon black, zeolites, clay materials, phyllosilicates, wax, paraffin, salts, metals, metal compounds, soluble organic compounds such as e.g. polyvinylpyrrolidone or polyethylene glycol and the like.
 8. The method according to claim 6 or claim 7, **characterized in that** the fillers are removed from the matrix by washing out with water, solvent, acids, or bases, or by oxidative or non-oxidative thermal decomposition.
 9. The method according to any of claims 6 to 8, **characterized in that** the fillers are present in form of powders, fibers, wovens, nonwovens.
 10. The method according to any of claims 6 to 9, **characterized in that** the fillers are suitable to cause foam formation in or on the polymer film.
 11. The method according to any of the previous claims,

characterized in that the material is subjected to an oxidative and/or reducing aftertreatment subsequent to pyrolysis and/or carbonization.

12. A porous, carbon-based material that is producible in accordance with the method according to any of the previous claims.