

Chapter 2

Carbon Gels and Their Applications: A Review of Patents

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2.1 Introduction

Scientific and technological advances over the past four decades have led to an increase in the demand for new technologies as well as improvements in the existing ones. In many cases these improvements involve the development of new materials. In particular, carbon has attached a great deal of interest, since natural carbon materials have extraordinary properties that confer on them a great potential for different applications. However, its impurities and a lack of control over its properties have led to its replacement by synthetic carbonaceous materials. These synthetic materials share the same structure as materials obtained from natural sources of carbon, with the added advantage that their chemical and porous properties can be adapted to the requirements of a particular application. Synthetic carbonaceous materials include carbon gels, porous materials composed of primary particles that are interconnected to create a three-dimensional network structure.

The formation of the polymeric structure depends to a great extent on the conditions established in the synthesis process, which in turn define the properties of the carbon gels. Therefore, the main advantage of carbon gels is that, by appropriately selecting the process conditions, the properties can be controlled and designed to achieve the optimum behaviour of carbon gels for a wide variety of

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scientific fields and applications [1, 2]. Attracted by the great versatility of carbon gels, researchers around the world have focused on this type of material. However, despite its great commercial potential, the number of patents in relation to the amount of research being carried out and published is not very high (1 patent per nearly 100 research articles). These data are very revealing and must prompt the reader to ask himself the following questions concerning the low number of patents reported: is the synthesis process of carbon gels mature enough to be transferred to the industry? Have carbon gels really a wide sales market and can they be offered at competitive prices?

In this chapter, an attempt to write a review of patents on the synthesis and applications of carbon gels has been made in order to bring some enlightenment to these questions.

2.2 Carbon Gels

The first patented carbon gel was reported in 1989. Inspired by the synthesis of inorganic silica gels, Pekala and co-workers patented the methodology sol–gel for synthesizing organic gels, which are the precursors of carbon gels [3]. The methodology consists of provoking a polymerization reaction in which a liquid gradually condenses from a stable suspension of colloidal solid particles (sol) to create a three-dimensional porous network formed by polymeric chains in a liquid medium (gel), as shown in Fig. 2.1.

In this first patent, a polymerization reaction occurs between resorcinol and formaldehyde under alkaline conditions, i.e. in a reaction media composed of water and sodium hydroxide [3]. This reaction involves two main stages: (i) an addition reaction and (ii) a condensation reaction. Resorcinol is a trifunctional benzyl compound with two hydroxyl groups in positions 1 and 3 which allows

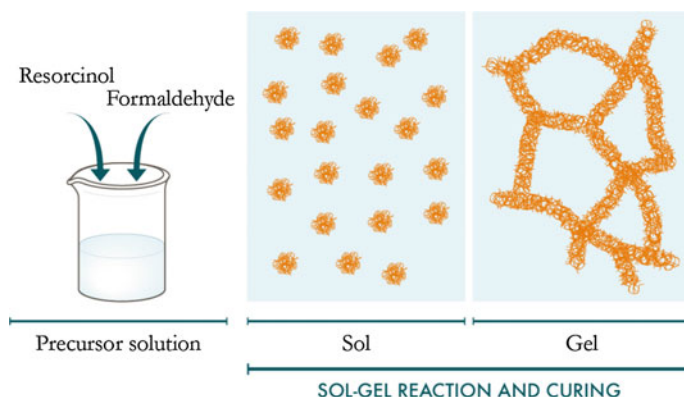


Fig. 2.1 Synthesis of organic gel by the sol–gel methodology

formaldehyde to be added in positions 2, 4 and 6 [3, 4]. In the presence of a basic catalyst, resorcinol anions are formed due to the abstraction of hydroxylic hydrogens. These anions are more reactive than resorcinol itself, which favours the addition of formaldehyde to form hydroxymethyl derivatives, as shown in Fig. 2.2.

At the same time as the addition reaction, condensation occurs, as shown in Fig. 2.3. The hydroxymethyl derivatives lose OH^- groups to form benzyl-type cations. These cations react with other benzene rings, giving rise to methylene and ether bonds [5]. Polymeric particles are then formed. These primary particles aggregate and cross-link with each other via polymer chains to form a three-dimensional porous network in a liquid medium.

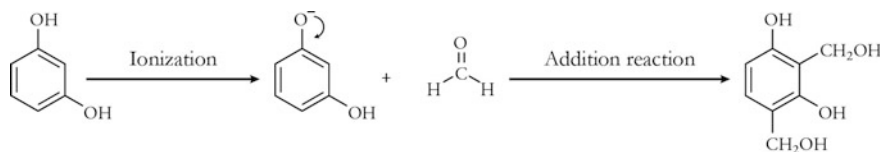


Fig. 2.2 Scheme of the addition reaction between resorcinol and formaldehyde

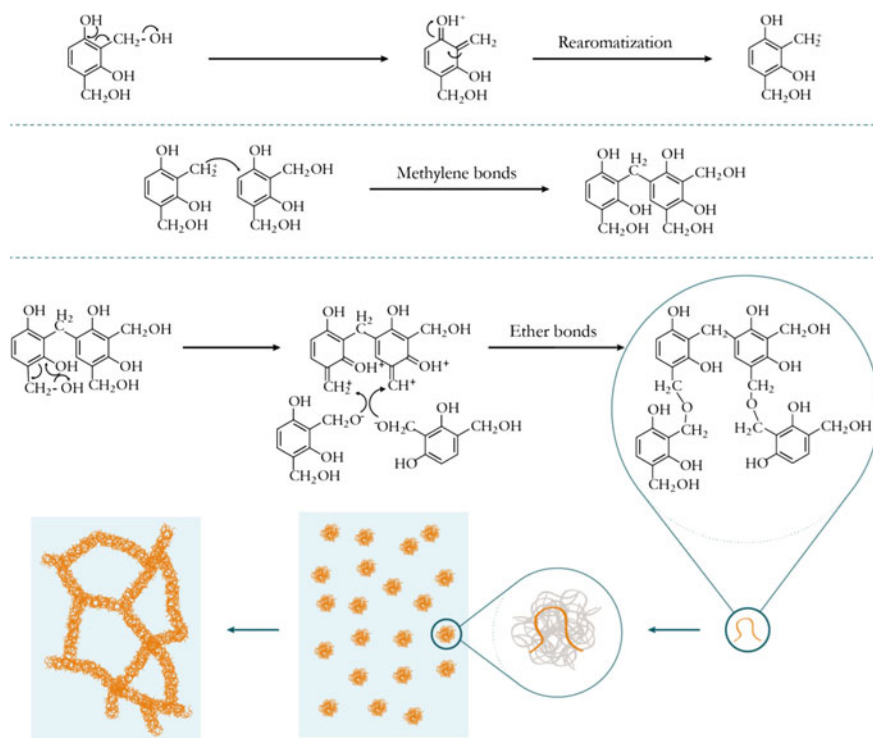


Fig. 2.3 Scheme of the condensation reaction between resorcinol and formaldehyde

The formation of primary particles causes the fluidity of the precursor solution to decrease. The time between the start of the reaction until the moment at which the solution loses fluidity is known as gelation time, while the exact moment at which the gel is obtained is called gelation point. After the gel point has been reached, the solid immersed in the liquid structure continues to evolve. This stage is called curing and during this stage the material hardens due to the simultaneous effect of cross-linkages between the polymer chains and to the partial evaporation of the solvent, which is mainly water. Once the sol–gel reaction and curing stages are completed, optional acid-washed steps can be performed in order to increase the degree of cross-linkages [3].

Organic gels obtained after the sol–gel reaction and curing stage must be dried to completely remove the solvent still embedded inside the structure. The first drying method used for the synthesis of organic gels was supercritical drying. In this method the solvent is replaced by carbon dioxide (CO_2) which is subsequently disposed of in a process carried out at high pressure [3]. Due to the low solubility of CO_2 in water it is necessary, prior to the drying, to replace the water used as solvent in the precursor solution with an organic solvent such as acetone (Fig. 2.4). In order to completely remove the residual water, multiple exchanges with fresh acetone are needed. After the solvent has been exchanged, the gel is dried by supercritical drying. First, the acetone is replaced with liquefied carbon dioxide and then the gel enclosed inside a vessel at 900 psi and 14 °C. Sequentially, the pressure is slowly reduced in order to remove the carbon dioxide that was previously introduced [6].

Dried organic gels obtained by supercritical drying are known as organic aerogels and can be subjected to thermal treatments to stabilize the material and modify its properties. Depending on the treatment conditions, oxygenated and hydrogenated groups can be removed, which gives rise to a carbonaceous material known as carbon aerogel.

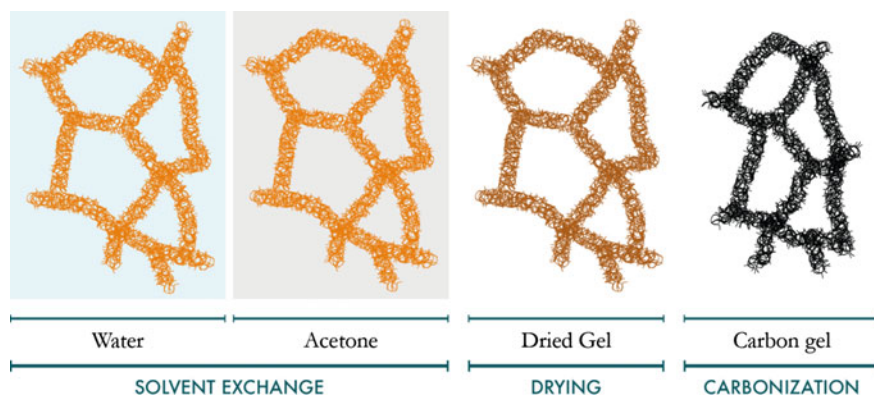


Fig. 2.4 Solvent exchange and drying stage in the synthesis of organic gel

Carbon aerogels obtained by this method are unique and have physicochemical properties, such as a high specific surface area and pore volume, a low density, an excellent electrical conductivity and a high purity. These properties can be controlled and designed to fit the requirements of a specific application. Furthermore, carbon gels can be synthesized in the form of monoliths, powders, microspheres or thin films, with high packing densities [1]. These characteristics go some way to explain why carbon gels have acquired a high commercial value and why the interest to synthesize them at industrial scale has increased over the last decades.

However, as explained above, the most common process for synthesizing carbon aerogels involves several steps: sol–gel reaction, curing, acid-wash, solvent exchange, supercritical drying and carbonization. Some of these stages are rather expensive and difficult to handle, which makes the process unfeasible at an industrial scale. Consequently, over the last 25 years great efforts have been made to overcome the main drawbacks of this process with the two-fold aim of: (i) achieving a feasible industrial synthesis process and (ii) improving the properties of carbon gels in order to increase the number of applications for which they can be used and increase their marketability.

2.3 Improvements in the Synthesis Process of Carbon Gels

The main stages involved in the most common method for synthesizing carbon gels are both costly and time-consuming. On the one hand, the polymerization reaction between resorcinol and formaldehyde is spontaneous but slow, and to promote it is essential to heat the precursor solution up. The most widely used process involves heating in electric furnaces to a temperature not exceeding 100 °C to prevent the precursor solution from boiling. This method requires several days for the sol–gel reaction and curing stage. The use of electric furnaces is very costly due to high level of energy consumption and long periods of time required to produce the organic gel. On the other hand, supercritical drying not only requires extreme drying conditions entailing a substantial increase in production costs, but usually several solvent exchange steps are also needed. These factors are some of the main obstacles to the implantation of this synthesis process at industrial scale. Consequently, research in this field is being carried out to develop easier, faster and cheaper methods of synthesizing carbon gels in order to make them more attractive and competitive than other commercial carbonaceous materials.

2.3.1 Drying Methods

The structure of carbon gel is reflected in the structure of dried gel which, in turn, is determined by the organic wet gel. These features can be created during the polymerization reaction but, if care is not taken in the removal of the solvent, the

structure cannot be preserved. During drying, surface tensions occur in the liquid–vapour interface generated onto the surface of the pores [7]. As a result, capillary forces appear. If the mechanical strength of the polymer structure is not high enough to counteract these capillary forces, the structure could completely collapse, giving rise to non-porous materials [4]. From the equation of Young–Laplace shown in Fig. 2.5 and given that pores are spherical, it can be inferred that the degree of collapse will depend on (i) the specific surface energy, (ii) contact angle between the porous structure and the solvent and (iii) pore size. Accordingly, the drying must be conducted under conditions designed to avoid the collapse of the polymeric organic wet structure and to enable the dried gel to retain its original surface structure and porosity [8]. It has already been explained that this can be achieved by supercritical drying, which give rise to organic aerogels. However, the high level of energy, time and cost consumption involved have led researchers to seek other drying methods [9].

Freezing-drying has been widely patented as a drying method for organic gels that can avoid the collapse of the polymeric structure. Materials obtained by this method are known as organic cryogels. The concept of the freezing-drying method is to promote nucleation rather than crystal growth [8]. By freezing the wet gel a fine ice crystal structure within the primary particles is formed due to the wide-spread nucleation of ice crystals. As the solvent is cooled, the solvent undergoes crystallization until the eutectic point is reached. At this point, it undergoes the transition from a liquid to a solid until complete freezing is achieved [8]. After the material has been frozen, the solvent is removed by sublimation under low pressure for 3 days [7, 9, 10]. Sublimation is performed in a lyophilizer pre-cooled at a temperature that ranges from -10 to -50 °C, depending on the type of solvent employed [8, 9, 11]. Liquid nitrogen or ethanol cooled in dry ice are usually used to freeze the solid [8].

As inferred from several patents, freezing-drying has an advantage over supercritical drying as solvent exchange can be avoided if the proper solvent is used [7]. Instead, wet gels can be filtered or decanted in order to remove any excess dis-solvent before freezing [11]. These simplifications have made it possible to commercialize carbon cryogels. An example of this is Energy2 Technologies Inc.,

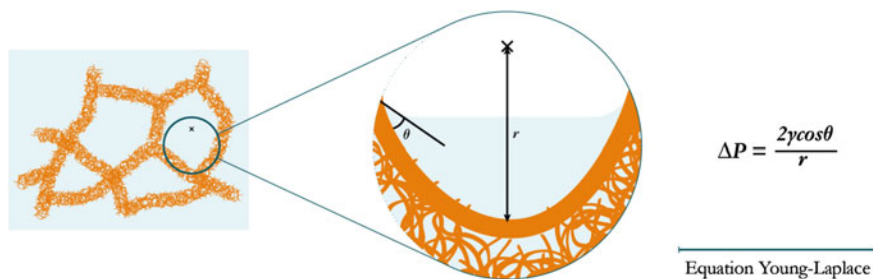


Fig. 2.5 Scheme of capillary forces on porous materials

which produces uniquely tailored carbon cryogels at costs that are competitive with the traditional carbons used in high performance applications.

Nevertheless, although supercritical and freezing drying are efficient methods for the fabrication of organic porous materials that remain porous after pyrolysis, both the methods are rather tedious, expensive and difficult to handle [12]. In order to further simplify and reduce the cost of these drying processes, new methods of producing carbon gel that do not require the step of supercritical or freezing drying have been reported. For example, wet gels can be dried in a vacuum by heating at a temperature between 50 and 100 °C for about from 2 to 20 h [7]. Centrifugation followed by evaporative drying can be also used as a drying method. Obviously, the structure of the gel must be able to withstand the centrifugation process. The pressure differential method can also be applied in order to force the liquid out of the structure by displacing it with gas, a vacuum [13, 14] or another liquid solvent [7]. Both centrifugation and the pressure differential method remove most of the liquid but not all and hence, post-evaporative drying methods are needed to completely remove the solvent [7].

These latter methods have led several researchers to look for a drying method based exclusively on the direct evaporation of the solvent. The first subcritical drying method, in which a simple air drying procedure was applied, also involved several solvent exchanges with different solvents such acetone, cyclohexane [13] or n-pentane [15] prior to the drying step. Subsequently, evaporative drying without a solvent exchange step was patented. First, drying was performed over a period of 40 days in order to avoid shrinkage [16]. However, it was observed with time that evaporative drying was also feasible in just 3 days [4, 17], without triggering the collapse of the structure. The materials obtained by this drying method are known as organic xerogels and can be obtained by a simpler, quicker and less expensive process making it more likely to be adopted at industrial scale.

It should be pointed out, however, that the synthesis of organic xerogels undergoes substantial shrinkage and even cracking of the structure upon drying at ambient conditions [18]. As indicated in Fig. 2.5, the degree of shrinkage depends on the specific surface energy, contact angle between the porous structure and the solvent and pore size. In the particular case of xerogels, the two first terms remain constant. Hence, shrinkage depends on the shape of the polymeric structure. Materials with a lack of sufficient mechanical strength to withstand the stresses arising during drying will tend to shrink and crack [4]. However, this drawback can be minimized by selecting the appropriate conditions for the previous sol–gel reaction and curing stages in order to obtain materials whose mechanical strength counteracts the capillary forces and avoids or reduces the risk of collapse.

2.3.2 Heating Methods

Typically, the precursor solution is sealed in a heat-resistant container, made of polypropylene or glass, which is placed in a thermostat-controlled oven, where the

sol–gel reaction and curing stages are performed. The recent advances in drying processes now allow the drying to be carried out in the same electric oven. To this end, is necessary that the container enables the removal of the solvent [4]. However, the use of electric furnaces in all three main stages of the synthesis process is still very costly due to the high level of energy consumption and long times required to produce the organic xerogels (from 4 to 7 days). In order to obtain more competitive materials, some patents employ faster and cheaper heating sources.

Electrochemical processes can be used as methods to initiate the polymerization reaction [18]. Once the reagents involved in the sol–gel reaction have been selected and mixed in the appropriate proportions, two electrodes (cathode and anode) are immersed in the solution. A DC electric current is then supplied via the electrodes at room temperature for a period of 1–3 days. The electric current is in the range of 0–8 A with a voltage ranging from 0.01 to 60 V [18]. The current applied is essential for tailoring the final properties of the carbon gels. For example, an increase in the voltage results in carbon gels with a lower surface area [18].

Although to the best of our knowledge, there are no patents on the use of ultrasonic radiation as a heating method for the synthesis of carbon gels, this particular method has been reported in scientific journals [12, 19, 20]. This in itself makes it worthy of mention in this chapter. Ultrasonic radiation was first applied to perform drying. The use of this heating source avoids the solvent exchange stages and the need for high operating pressures. However, it is a long drying procedure which takes about 34 h. Years later, the polymerization reaction was also accelerated by ultrasonic radiation. This strategy was found to be very helpful for increasing reaction rates, products yields and for shortening the reaction time required.

Microwave radiation has been reported to be a very efficient heating source for synthesizing carbon xerogels [12]. At first, microwave heating was used only in the drying stages but it was soon realized that this technology was applicable to the whole process [21]. The general idea of this method is to apply a controlled microwave radiation to the precursor solution in order to promote polymerization, curing and drying. Carbon xerogels with similar characteristics to conventionally synthesized xerogels are obtained, but with a considerable saving of time, i.e. up to 90% (3–4 h under microwave radiation compared to several days by conventional heating) [21, 22]. In addition, there are several other advantages to be had by using microwave technology to fabricate carbon xerogels. In microwave heating it is possible to determine the different stages of the process: sol–gel reaction, curing and drying. This make it possible to allows control the viscosity of the reaction media which, in some cases, is essential to obtain organic xerogel in a specific form (i.e., sphere, monolith, film, etc.) [23].

Nowadays, microwave heating is presented as the most effective and economical method for synthesizing organic xerogels at an industrial scale. It involves a simple and fast method from which very competitive and high added value materials can be obtained. A good example is afforded by Xerolutions Ltd. which, since 2015, has been commercializing carbon xerogels synthesized by microwave radiation.

2.4 Improvements in the Properties of Carbon Gels

The main advantage of carbon gels is that it is possible to tailor their properties to meet the requirements of the final application. The properties can be designed by selecting the appropriate synthesis conditions. This includes, but is not limited to: (i) the nature and concentration of the main reagents, (ii) the introduction of doping agents or additives at different stages of the synthesis process and (iii) the application of thermal treatments.

2.4.1 *Nature and Concentration of the Main Reagents*

The synthesis of carbon gels begins with the preparation of an aqueous solution containing hydroxylated benzenes, aldehydes, solvents and, when necessary, a fourth compound, known as the catalyst, which regulates the pH and catalyses the reaction. The nature and concentration of these reagents play a key role in tailoring the properties of organic gels.

As explained above, the first and also the most commonly used reagents for the synthesis of carbon gels are resorcinol and formaldehyde. Their concentration has a direct effect on the final porous properties of carbon gels. Formaldehyde is responsible for the formation of crosslinkages between primary particles. An increase in the concentration of formaldehyde leads to highly branched structures of high mechanical strength. These structures are able to counteract the surface tension generated during drying, so that shrinkage is minimized and the carbon gels obtained have higher pore volumes [2, 24].

The polymerization reaction between resorcinol and formaldehyde is a spontaneous but slow reaction. Therefore, a catalyst is often added to the precursor solution to initiate the sol–gel reaction and modify the final formation of the polymeric structure. Catalysts can be basic such as alkali carbonates, acetates or hydroxides [3, 9, 10, 15, 25] or acidic, which includes, among others, hydrochloric acid, acetic acid, hydrobromic acid, uric acid, phosphoric acid or sulfuric acid [7, 11, 26, 27]. In general, regardless of its nature, increasing the amount of catalyst substantially reduces the time required for the polymerization reaction to run its course [7]. There is, however, a maximum allowable amount of catalyst that can be added to each particular precursor solution, since an excessive reduction in the reaction time could give rise to non-porous materials.

The concentration of the catalyst is related to the pH of the precursor solution, one of the most important variables in the synthesis of carbon gels, as it has a strong influence on their final porous properties [4, 8]. Its effect can be explained in relation to the polymerization reaction between resorcinol and formaldehyde. The reaction starts with the abstraction of the hydroxyl hydrogen from the resorcinol, as previously shown in Fig. 2.2. The addition of a basic catalyst promotes the abstraction of hydroxyl hydrogens and in turn, the formation of resorcinol anions.

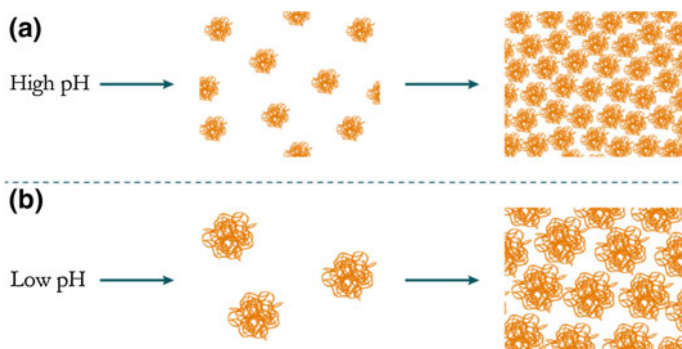


Fig. 2.6 Formation and growth of primary particles depending on the pH of the precursor solution

Therefore, increasing the concentration of catalyst (i.e., raising the pH value) causes an increase in the number of resorcinol anions to which the formaldehyde can be added. As the number of resorcinol anions increases, the addition reaction proceeds faster, giving rise to the formation of a large number of small primary particles [24]. Polymeric structures with a large amount of small primary particles lead to organic gels with narrow pores (Fig. 2.6a). Conversely, a low catalyst concentration (low pH value) generates a small number of resorcinol anions. The addition of formaldehyde takes less time than when adding more catalyst. As a result, a condensation reaction is promoted and the medium persists longer in the nucleation stage, favouring the formation of structures with a small number of large primary particles. These polymeric structures lead to organic gels with pores of larger size (Fig. 2.6b).

In contrast to the base-catalyzed route, which is based on activating the aromatic ring (Fig. 2.2), the acid-catalyzed route is based on accelerating the reaction by increasing the electrophilicity of formaldehyde [28]. The protonation of formaldehyde is followed by a nucleophilic attack on the resorcinol, leading to its hydroxymethylation. The hydroxymethyl groups formed are then protonated and react with other benzene rings giving rise to methylene and ether bonds. The acid-catalyzed process yields organic gels with a similar chemical composition to that obtained using basic catalysts. However, variations in morphology have been observed due to differences in the gelation mechanisms. With acid catalysts, the formation of the hydroxymethyl derivative occurs more slowly and, as a result, structures with a larger pore size are obtained [28, 29].

The reaction medium is also an important factor in the synthesis of carbon gels, particularly the specific surface energy, which is one of the factors governing the capillary forces, as previously explained (Fig. 2.5). Several solvents are available including deionized water, acetone, cyclohexane, methanol or ethanol. Each of these compounds has a different surface tension and therefore, the behaviour during the curing and drying stages will result in different pore structures of the final materials. Water exhibits the highest surface tension value (72.8 mN/m vs. 23.7,

25.5 and 22.6 mN/m for acetone, cyclohexane and methanol, respectively), causing a further collapse of the polymeric structure when the solvent is removed. Some patent authors have demonstrated that the degree of collapse when using water can be minimized by adding other solvents or mixtures of them to assist the polymerization reaction or enhance certain useful properties of the carbon gels. For example, small concentrations of alcohols such as ethylene glycol, propylene glycol or glycerine (between 3 and 13% by weight of the total solution [7]) can be added to reduce the average pore size and to increase the strength of the polymeric structure. However, adding alcohol or increasing alcohol content tends to increase the gelation time. In order to minimize this effect, the concentration of the other reagents (hydroxylated benzene, aldehyde and catalyst) can be modified to overcome the effect of the alcohol.

Despite its high surface tension value, water is the least expensive reaction medium and therefore, the most preferred for synthesizing carbon gels. The water concentration exercises a significant influence on the meso–macroporosity of organic gels, due to the number and size of the primary particles formed during the polymerization reaction [5, 30]. For the same volume of precursor solution, a decrease in the concentration of water entails an increase in the concentration of resorcinol and formaldehyde and the higher the concentration of resorcinol, the greater the number of anions generated. In this way a large number of small primary particles are formed, leading to materials with smaller pores (mesoporous materials). As the concentration of water increases, i.e. the resorcinol-formaldehyde content decreases, fewer primary particles of larger size are obtained, giving rise to materials with larger pores (macroporous materials). However, if the water concentration is too high, the number of primary particles will be so small that gelation will not occur [5].

Although resorcinol and formaldehyde are the most common reagents, other potential combinations have been also patented, including hydroxylated benzenes from the group comprising phenol, catechol, hydroquinone and phloroglucinol or a mixture of them [3, 7, 8]. Partially pre-polymerized forms or aromatic compounds such as phenolic resin [27] or melamine [26], respectively, can be also used. Alternatively, formaldehyde can be replaced with furfural or other saturated aldehydes [7, 8, 27].

The nature and concentration of all reagents plays a fundamental role in the synthesis of carbon gels and, particularly, in designing their final properties. This gives an idea of the complexity and at the same time the versatility of the process, since each variable can modify the effect of the others. Therefore, the choice of a suitable combination of reagents is essential for the sol–gel reaction to take place properly and for controlling the properties. Some patented examples that illustrate the importance of preparing an appropriate precursor solution are described in detailed below.

2.4.1.1 Melamine Formaldehyde Aerogels

As explained above, the synthesis process begins with heating the precursor solution that contains resorcinol (R), formaldehyde (F), water and a basic catalyst. As the reaction occurs, the precursor solution turns a different colour. As a result, dried RF organic aerogels become dark red in colour and have a large absorption coefficient within the visible spectrum. The colour of the RF aerogels is a result of oxidation products formed during the polymerization, such as quinones [26]. This fact limits the use of the RF aerogels for certain optical applications where the material needs to transmit light and be non-absorptive in the visible spectrum. In order to address this problem, other reagents, which give rise to colourless organic gels, can be used. An example of this is found on the patent literature, in which resorcinol is replaced by melamine [26].

The removal of one of the main reagents to obtain a transparent material requires modifications of certain parameters governing the process, such as time and temperature of synthesis, type of catalyst and concentration of the reagents. Thus, the process for preparing melamine formaldehyde (MF) aerogels differs from that used to prepare RF aerogels. Melamine (M) and formaldehyde (F) are first dissolved in an aqueous solution containing the basic catalyst. Unlike RF aerogels for which the R/F molar ratio is usually fixed at 0.5, MF aerogels are synthesized using a M/F molar ratio of 0.27 [26]. As mentioned above, an excess of formaldehyde favours cross-linkages between polymeric chains and a more reinforced structure is obtained. Because of the limited water solubility of crystalline melamine, the precursor solution should be heated at 70 °C for 15 min until it becomes clear. The solution is then cooled to room temperature and the final pH value is adjusted by adding an acidic catalyst. In order to obtain a transparent material, the pH value must be within the range of 1–2. In contrast to the conventional synthesis of RF aerogels, acidic conditions are necessary for MF aerogels to promote the condensation reaction which leads to the formation of gel. Furthermore, the pH is the most important variable for controlling the transparency of the material. The temperature and duration of the synthesis of MF aerogels depend on the percentage of solids in the precursor solutions. Solutions with a high percentage of solids ($\geq 20\%$ wt.) become gel in 48 h at room temperature, while solutions with a low percentage ($\leq 7\%$ wt.) need to be heated up to 90 °C for 4 weeks [26]. Then the samples are cured at 90 °C for 5 days.

Another advantage of this process is that the acid-wash stages can be removed, since it is the excess of formaldehyde that provides additional crosslinkages. Finally, the wet MF aerogels are directly subjected to solvent exchange, drying and carbonization processes. The materials thus obtained exhibit similar properties to those of RF aerogels, but in addition they are transparent and, hence, useful in optical applications.

2.4.1.2 Phenolic-Furfural Aerogels

The growing interest in using aerogels in a wide variety of applications, either in organic or carbon form, has led to further developments with these materials with the focus on reducing costs and improving their properties. To achieve this replacement with less expensive reagents may be a reasonable alternative. Amongst all the possible reagents available, phenolic-furfural mixtures have been used in patents as precursors for the synthesis of organic aerogels with promising results [16, 27].

Phenolic-furfural aerogels are prepared by mixing phenolic novolak resins and furfural in equal proportions. In this synthesis process, propanol and phosphoric acid are used as solvent and catalyst, respectively [27]. Phenolic novolak is a low molecular weight polymer derived from the acid-catalyzed reaction of a molar excess of phenol with formaldehyde. In order to promote the sol-gel reaction, furfural must be added. In fact, the polymerization reaction occurs between aromatic rings of phenolic resin and the aldehyde group on furfural. The sol-gel reaction, curing and drying are performed following the method used for RF aerogels. However, these materials are particularly more efficient than conventional aerogels, as the use of propanol as solvent allows direct exchange with CO₂ prior to the supercritical drying step. Hence, there is no need for further solvent exchanges [16].

2.4.1.3 Phenol-Formaldehyde Aerogels

Even through phenolic-furfural mixtures lead to well-developed porous structures, furfural is more expensive than formaldehyde, which counteracts the costs saved by replacing resorcinol with phenol [17, 25]. Furthermore, the handling of furfural is more problematic than formaldehyde and its use is not desirable in industrial scale processes [17]. It is more profitable to obtain porous materials based on phenol formaldehyde (PF) precursor solutions. PF organic gels can be synthesized by the sol-gel reaction between phenol and formaldehyde using n-propanol as solvent and hydrochloric acid or sodium hydroxide as catalyst [17]. By means of this formulation, the sol-gel reaction, curing and drying stages can be performed following the method used for RF aerogels.

Resorcinol can also be replaced by phenol to give rise to organic xerogels, which are easier to synthesize than carbon aerogels. In this case, water and sodium carbonate are used as solvent and catalyst, respectively. However, it has been demonstrated that additives, such as cationic surfactants, are also needed in order to avoid shrinkage of the polymeric structure [25]. Moreover, it should be noted that only up to 70% of resorcinol can be replaced by phenol. Above 70%, the precursor solution precipitates and hence, sol-gel reaction does not occur properly [12]. Furthermore, the greater the amount of phenol used to replace resorcinol, the greater the amount of additive needed to obtain a well-developed porous structure [25].

2.4.2 *Introduction of Doping Agents and Additives*

Regardless of which precursors are used to synthesize carbon gels, other treatments can be employed to modify one or more properties and to fit them more accurately to the requirements of a specific application. For example, redox reactions, charge transfer, the wetting process, blockage of reactive sites, etc., are used in various applications. Hence, not only the porous properties but also chemical processes play an important role due to interactions between the fluids in the applications and the surface of the carbon gels. Doping carbon gels with different species or introducing additives into the precursor solutions are common processes for modifying the porosity and the chemical nature of carbon gels. Some of these processes have been patented due to the advantages they offer compared to the conventional synthesis process. Enlargement of the surface area, modification of the functional groups at the surface or enhancement of electrical conductivity are some of ways in which the gels can be modified [14, 31].

As inferred from several patented methods, doping agents can be incorporated into the carbon structures at various stages of the process as long as the doping agent is compatible with the process: (i) during the polymerization stage, (ii) in the polymer wet, dried or carbonized gel or (iii) during carbonization process.

Doping agents can be added to the precursor solution prior to gelation, followed by the conventional synthesis process [8, 14, 32, 33]. Other methods may involve previous ultrasonic water bath heat treatment in order to promote the polymerization reaction by high-intensity sonication until gelation is achieved. Sol-gel reaction and curing can be then continued as in the conventional method [16]. However, this technique exhibits some drawbacks as the doping agent may remain encapsulated inside the porous structure, particularly into closed pores, becoming inaccessible [34].

Another technique involves the impregnation of the wet, dried or carbonized gel in a solution containing the doping agent [35]. Several methods can be applied such as impregnation in a solution containing an excess of the doping agent, wet impregnation incipient [8], chemical vapour infiltration [32], ion adsorption, ion exchange or physical mixing [36]. Among all, impregnation is the most commonly used. The degree of doping depends on the method selected, the doping agent used and the structure of the carbon gel. In these techniques, it is necessary that the doping agent is dispersed in a solution that can then diffuse into the pores of the carbon. Doped organic gels can then be carbonized, leading to a coating of dopant agent on the inner surface of carbon gels, i.e. inside the pores [8]. However, the tortuosity in low permeable carbon gels may present significant experimental difficulties for incorporating into the structure of carbon gels certain doping agents, such as metal nanoparticles, particularly when have been synthesized as monoliths [33]. In these cases, it may be more convenient to tailor macroporous carbon gels in order to facilitate the incorporation of the doping agents.

Furthermore, the introduction of doping agents inside the porous structure, might lead to a decrease in surface area and total pore volume. This effect is enhanced

Table 2.1 Improvements in the properties and applicability of carbon gels by the incorporation of a doping agent and additives

Doping agent	Properties modified	Application	References
Carbon forms: Graphene, fullerenes, carbon nanotubes and fibres	Electric and mechanical properties Internal surface area Enhances metal doping	Energy storage Catalysis Adsorption	[16, 31, 32, 37–41]
Inorganic materials: Silica gels and ceramic	Porous and mechanical properties Thermal conductivity	Thermal insulation	[14, 42]
Metals: Ni, Pb, Pt, Rh, Ti, Cu, Ag, etc.	Electric properties Chemical properties (reactivity)	Energy storage Catalysis	[8, 33, 34, 36, 43–45]
Functional groups: O, N, S, P, B, F, etc.	Chemical properties (hydrophilicity, reactivity, etc.) Enhances metal doping	Energy storage Catalysis Adsorption	[6, 8, 46]
Additives: Surfactants (anionic, cationic or nonionic)	Porous and mechanical properties		[7, 11, 14, 25]

when the impregnation is carried out on dry samples, prior to carbonization, due to the subsequent drying of the solvent containing the doping agent. The organic gel is not able to counteract the capillary forces produced during this second drying process and shrinkage occurs [8]. The decrease in pore volume can also be produced due to the incorporated doping agent occupying pores within the pore structure.

Impregnation can be performed either on previously milled material or to non-milled material. Depending on the agent used for doping it will be better use one type of material or another. For example, it has been reported that a greater degree of manganese can be incorporated into a milled carbon gel than into non-milled samples, while the reverse case was observed with nickel [8].

In other words, the effect of doping depends to a large extent on the type of doping agent used. In the patent literature numerous doping agents used to improve the properties of carbon gels can be found (Table 2.1). The most relevant are described below.

2.4.2.1 Carbon Gels Doped with Other Forms of Carbon

Forms of carbon are generally added to precursor solutions prior to the synthesis of organic gels. Graphene, fullerene, carbon nanotubes, or carbon fibres are the most commonly used carbon dopants.

Doping with graphene can be carried out with non-functionalized graphene such as graphene oxide (GO) or other functionalized graphenes such as carboxylated graphene. However, graphene oxide is more common as the hydrophilic groups on

its surface make it easy for it to be dispersed in water [39]. Indeed, GO nanosheets are stable in an aqueous solution as a result of ionization of the carboxylic acid and phenolic hydroxyl groups that are known to be present on the GO sheets. The most common method to produce GO is by the Hummers method in which is suspended in a solution by ultrasonication. This solution can be used as the solvent in the synthesis of carbon gels [39]. Doping carbon gels with graphene allow more control over the density, shape, electric conductivity and internal surface, so that the resulting material displays improved electrical and mechanical properties [38]. This not only avoids shrinkage during drying but also leads to materials that are able to withstand harsher industrial conditions [39]. Furthermore, graphene can improve the dispersion of other doping agents, such a cationic metal, resulting in a material that is especially useful in catalytic applications [40]. Likewise, it has been reported that these materials have excellent adsorption properties. In fact, oil absorption on a graphene-doped carbon gel can reach 21–70 times its own mass [38]. Accordingly, carbon gels containing graphene, open up a whole new interesting range of possibilities for their application.

Fullerenes have great potential for use in energy storage devices due to their ability for become charged both on and into the ball. However, the balls are insulators and charges are not readily transported inside pure-fullerene solids. Hence, the idea of using carbon gels as a support for fullerenes has attracted the attention of researchers and a synthesis process has already been patented [32]. The porous structure of carbon gels enables fullerene molecules to be deposited on the surfaces of the pores, leading to an increase in surface area. These carbon gels are low-density materials and excellent mechanical and conductive supports. As a result, lightweight composites with a high electrical conductivity, ideal for energy-storage applications, are obtained [32].

Carbon nanotubes are also commonly used doping agents in the synthesis of carbon gel due to their high strength and resistance to corrosion [31]. These features along with their large specific surface area, pore structure that is suitable for mass transport and good thermal conductivity properties can lead to composite materials with improved properties. The improvements achieved by the addition of carbon nanotubes allow carbon gels to be used in several applications with a better performance. For example, carbon gels doped with nanotubes have been patented as catalyst supports in fuel cells. The incorporation of nanotubes increases the oxygen reduction reaction [31]. Importantly, the catalyst material obtained is less expensive than commercial materials, which can significantly reduce costs and help to promote the commercial application of fuel cells. Carbon gels doped with nanotubes have also been patented as oil-absorbing materials. A small amount of carbon nanotubes leads to larger pores and, hence, the absorption rate is increased from 27 to more than 50 g/g (oil/doped carbon gel) [37].

Carbon fibres can also be added to the precursor solutions [16, 41]. This doping agent provides mechanical strength and electric conductivity to carbon gels, resulting in interesting materials for use as a functional material in aircraft and vehicles [41] or as electrode material in electrochemical devices [16].

2.4.2.2 Carbon Gels Doped with Inorganic Materials

Inorganic materials such as silica gels [14] have also been reported to be good doping agents. The addition of silica gel leads to really interesting materials for use as thermal insulators. Thermal conductivity decreases by as much as 30% when 50%wt. of silica gel is added [14]. Furthermore, the addition of reinforcing inorganic aerogel particles significantly mitigate shrinkage of organic aerogels that inevitably occurs during sol–gel processing and drying stages [14].

Carbon gels can also be produced by premixing the precursor solution with ceramic materials [42]. Ceramic materials offer internal support to carbon gels, which makes them suitable for use as electrode material [42]. Examples of effective ceramic materials include silica, alumina-silicates or glassy materials based on borate phosphates or silicates with alkaline earth or transition metals [42].

2.4.2.3 Carbon Gels Doped with Metals

Nowadays, several patents can be found on doping carbon gels with metals due to the great benefits this process offers in many applications. A feasible way to incorporate metals is by impregnation, in which carbon gels are exposed to a colloidal suspension containing the metal. Suitable metals include nickel, copper, platinum, palladium, silver, noble metals, etc. which can be added in elemental form, oxidized form such as oxides, salts, etc., or as part of a chemical compound or alloy [8, 36, 43, 44, 47]. Then, a thermal treatment is applied to reduce the doping agents to their metal state [45]. The maximum theoretical metal content that can be introduced into the precursor solution depends on the amount of water used in the synthesis and the solubility of the metal or metal compound [8, 33]. A metal content, expressed in terms of percentage weight of the total weight of carbon-doped gel, of up to 25% can be obtained depending on the metal precursor used and the post-thermal treatment applied [33]. The phase and crystal structure of the metal or oxide can be adjusted by controlling the temperature and time of the heat treatment [8]. Milling conditions to which the carbon gels are subjected are also relevant, as an excessive degree of milling, could result in a material with the metal filling the mesopores and not in the micropores [8]. Furthermore, a successful dispersion of the metal nanoparticles would be facilitated by the appropriate arrangement of the chemical anchoring sites inside the polymeric structure [34]. For example, the incorporation of functional groups [44] or the introduction of surfactant into the precursor solution could increase the number of anchoring sites, thereby facilitating the dispersion of metals [34].

Metals enhance electrical properties when incorporated into a carbon material, but doping with metals is commonly used to incorporate catalysts into the structure of carbon gels in order to enhance certain catalytic reactions. The catalyst can be deposited by co-precipitation, the urea method, induced hydrolysis reconstruction, the sol–gel technique, hydrothermal, microwave, ultrasound treatments and anion exchange reactions [36]. Regardless of the technique of deposition used, it is

essential to ensure an effective dispersion and tethering of the metal through the pores in order to significantly increase the catalytically active electrode surface and to avoid lixiviation of the metal during catalysis. This can be achieved by using a properly porous-tailored carbon gel. Microporosity on carbon gels favours the tethering and dispersion of transition metals [33], while meso–macroporosity facilitates the transport of molecules (fuels, oxidants reactants, etc.) to the active catalytic sites [44].

2.4.2.4 Functionalization

The main objective of functionalization is to introduce heteroatoms onto the surface of carbon gels. The most common functionalization methods are the incorporation of oxygen and nitrogen groups. However, recently the possibility of incorporating other heteroatoms onto the surface of the gels, such as sulphur, phosphorus, fluorine or boron, excited a great deal of scientific interest. Functionalization enhances the performance of carbon gels in certain applications, such as in some catalytic processes or energy storage systems. In the latter, interest has been especially intense due to the improvement in the interaction between the electrolytes and the surface of the carbon gels [6, 8].

Functionalization can be performed on the outer surface of carbon gels or the inner pore surface. There is a variety of techniques that can be applied independently or in conjunction, depending on the type of functionalization desired. Surface functionality can be modified by replacing the main reagents by others containing boron [48] or nitrogen [49] or by introducing additives [50]. Alternatively, the inner chemical surface of the pores can be adjusted by exposing the carbon gels to various gases or solutions at certain temperatures [8]. Functional groups can thus be incorporated into the carbon structure as substitutional atoms, during the polymerization or pyrolysis process or by means of a post-treatment process.

The term functionalization is known as oxidation when oxygenated functional groups are introduced [47]. The oxidation process can be performed with an oxidizing gas (ozone, oxygen, nitrous oxide, nitric oxide, carbon dioxide, etc.) or with oxidants aqueous solutions (sodium hypochlorite, hydrogen peroxide, ammonium peroxydisulfate, nitric acid, etc.). The presence of oxygen-based functional groups can affect the wettability and chemical and electrochemical reactivity of carbon gels, which is of great importance for establishing the electrochemical double layer generated in supercapacitors [46].

The process of incorporating nitrogen groups can be accomplished with various compounds such as nitric monoxide, amines or nitriles [15]. The degree of functionalization and the nature of the functional groups depend on the reactivity of the oxidant or dopant, the nature of the carbonaceous material and the temperature and treatment time. The increase in the number of functional groups favours the subsequent anchoring of metallic particles, property of great interest in catalyst supports [15]. Moreover, hydrophilicity, which is a property necessary when using the carbon gel as an adsorbent, can also be improved.

The incorporation of sulphur groups can be performed by post-synthesis treatments such as impregnation. The sulphonation patented process consists of bringing the carbon gel into contact with a concentrated solution of sulphuric acid [46]. After impregnation, a heat treatment is performed in order to decompose the functionalizing agent to give rise to sulphur trioxide, which is then released through the pores of the polymeric structure. Ultrasounds can be also applied before any temperature increase in order to accelerate the filling of the pores [46]. The introduction into the precursor solution of heterocyclic sulphur such as thiophenecarboxaldehyde can be also used [43]. Its aldehyde group also contributes to the formation of the structure by allowing thiophene-like functionalities to be retained inside mesoporosity. This is quite an interesting technique if further doping with Pt is performed, as the incorporated functionalities can bind to Pt nanoparticles from colloidal suspensions [44]. Another process involves the introduction of sulphur using gaseous agents such as H_2S or SO_2 under different heating conditions. However, this process has a major industrial disadvantage as the gases produced are toxic and its implementation is complex [46].

Phosphor-doped carbons are of interest for use as electrode materials in lithium-ion batteries [36]. Phosphorus impregnation can be performed by bringing the carbon gel into contact with a H_3PO_4 solution prior to carbonization. By this technique, the electrochemical capacity of the batteries can be enhanced due to the greater intercalation of lithium into the carbon structure [51]. Phosphoric acid can also be used as catalyst in the preparation of the precursor solution to obtain carbon gels doped with phosphor [36].

2.4.2.5 Introduction of Additives

Preservation of the pore structure of the gel during removal of the solvent is important. During drying, the gel can shrink substantially, leading to an increase in density of the final material or even to non-porous materials. In order to minimize this effect, some patents suggest the incorporation of reinforcing additives into the precursor solution so as to moderate shrinkage and densification [7, 11, 14, 25]. However, it should be noted that additives not only avoid shrinkage but can also alter the polymerization reaction and in turn the final properties. Indeed, additives can also precipitate at a certain pH value or even modify the initial pH value, which may lead to a poorer control over the final properties [11, 25]. Furthermore, depending on the processing conditions, a certain amount of additive may remain after drying. This can be a drawback for some applications in which organic gels are needed and other variables such as the concentration of the main reagents and/or the synthesis conditions may need to be adjusted to avoid shrinkage [7], or alcohol washing stages may need to be applied to remove the surfactant [25]. In the case of carbon gels, this inconvenience disappears as additives can be removed during carbonization process [7, 8]. Hence, it is essential to select the appropriate nature and concentration of the additive used.

2.4.3 Thermal Treatments

Thermal treatments such as carbonization or activation are well-known techniques, used in multiple processes in order to obtain carbonaceous materials from different precursors. Due to pre-gel knowledge about these processes, the number of patents regarding standard thermal treatments applied in the synthesis of carbon gels is quite limited. However, these processes are of great importance and deserve to be mentioned in the present chapter.

2.4.3.1 Carbonization

Once dried organic gels have been obtained, carbonization must be applied in order to produce the final carbon gel. This process consists in bringing the organic gel into contact with an inert gas in a tube furnace at high temperature. Nitrogen, helium or argon are usually used as carrier gas and constant and moderate flows are selected according to the amount of sample and the size of the tube furnace. Temperatures between 600 and 1000 °C are generally used with slow heating ramps to prevent excessive shrinkage of the structure as a result of the removal of the gases produced inside the material [8, 11].

The main aims of carbonization processes are first to stabilize the material, and second to increase the micropore volume and surface area and also to widen the narrow pores formed during the process of synthesis. During this process, non-cross-linked organic chains, labile oxygen and hydrogen surface groups are removed, due to breakages of the C-O and C-H bonds at low and high temperatures respectively, which results in thermally stable nanostructured materials made up mainly of carbon. Furthermore, the elimination of volatiles and labile matter leads to the formation of microporosity, mainly in the primary particles of the polymer, while the nanostructure developed during the synthesis of the organic gel usually remains intact during the carbonization step [4, 25]. Thus, microporosity can be controlled during the carbonization step and meso–macroporosity can be controlled during the synthesis of organic gels, which is a great advantage for the design and control of the porous properties of carbon gels [8]. This type of nanostructure endows the materials with a series of electrical, thermal and mechanical properties that are very useful in applications related to catalysts and energy storage.

Others gases such as fume of ammonia can be used during carbonization. In this case, in addition to the development of the microporosity, nitrogen functionalities are incorporated into the structure.

2.4.3.2 Activation

The carbonization process converts not only organic gels into carbon gels but also increases the surface area. However, certain applications, such as some energy

storage systems require very high areas and it is then necessary to apply other heat treatments. Activation processes can increase the surface area to 2000–3000 m²/g. Carbon gels can be also subjected to activation processes after or during the carbonization step. During activation, the volume of narrow pores created during the synthesis of the organic gel and/or the carbonization process is also increased. Therefore, it is very common to activate carbon xerogels for use in applications where besides narrow mesopores a high volume of micropores are also needed. It is generally accepted that there are two main types of activation: chemical and physical.

Chemical activation consists in bringing the carbon or organic gel into contact with an activating agent (phosphoric acid, zinc chloride, alkali carbonates, alkali hydroxides, etc.) at temperatures between 400 and 800 °C [11, 46]. After this heat treatment, the material must be washed to remove residual chemical agents and possible inorganic products generated in the reaction. This step is one of the main disadvantages of this type of activation, since in addition to lengthening the process, sometimes it is extremely difficult to completely remove all the traces of the residual activating agent.

Physical activation is the most common method and consists in bringing the material into contact with a gas (water vapour or carbon dioxide) at temperatures between 700 and 1000 °C [6, 8, 46]. Activation time and temperature have a big impact on the resulting activated carbon material as well as on the manufacturing costs. Increasing the temperature and time leads to higher activation percentages but also increases the cost by reducing the overall yield [8]. Carbon gels obtained by this method exhibit different porous properties to those obtained by chemical activation. Therefore, the final application of the activated carbon gels will determine which activation process will be more suitable.

2.5 Applications

Carbon gels have generated widespread interest over the past decades due to the possibility of designing their properties to fit the requirements of specific applications. The right combination of properties makes organic and carbon gels suitable for use in various applications, many of which have been patented. Some of the most outstanding patents are described below.

2.5.1 *Electronic and Energy Storage Applications*

Interest in electronic applications and energy storage has increased considerably in recent years because of the importance these devices have acquired around the world. In most of these applications carbon gels are used as electrode material. However, each of these devices operates differently, and hence carbon gels with

different properties are required for each application. In general, a high affinity between the carbon surface and certain particles that can be easily wetted by electrolyte is required for ion conduction and electrochemical reactions, while particles that repel electrolyte are convenient for gas diffusion channels [8, 52]. Furthermore, pore size also plays an important role, as carbon materials with small mesopores (less than 10 nm) may be useful to enhance the transport of ions and maximize power [8, 53]. In general, an optimized blend of micropores and mesopores within the carbon structure contributes to the enhancement of electrochemical performance in energy storage devices.

The use of carbon gels with a high density that are electrically conductive, dimensionally stable and machinable as electrode material in supercapacitors can increase specific capacitance considerably compared to that of conventional capacitors [6, 53]. This is because it is possible to design the properties of carbon gels. Capacitances increase with pore volume and surface area. Small mesopores and large micropores seem to be the ideal combination of properties as these pores are large enough for electrolyte ions to diffuse through and yet small enough to ensure that the material has a large surface area. However, should be noted that the surface area not only needs to be high (preferably of the order of 1500 m²/g) but also accessible, inasmuch that micropores that are too small may not be accessible to large electrolyte ions, especially cations [52, 53]. Therefore, an optimized structure will have large pores to act as a transmission and electrolyte transport pathway and fully accessible micropores for developing the highest specific capacitance.

Carbon gels with optimized properties for use as electrode material in different type of batteries are also expected to address the deficiencies provided by current commercial materials. In lithium-ion batteries, pore size distribution is important for both the storage capacity of the material and the kinetics and power capability of the system [36]. On the one hand, micropores with an average pore size smaller than 1 nm may create additional storage sites as well as lithium-ion diffusion paths, while surface areas smaller than 50 m²/g have shown even better efficiencies. On the other hand, mesoporosity provides pathways for electrolyte, the conduction of ions and electrons. Furthermore, mesopores are especially suited for doping, which has been demonstrated to improve the electrochemical capacitance of batteries [36, 51]. The use of properly designed carbon gels leads to efficiencies in the first cycle of more than 80%.

Metal–air batteries have a much higher theoretical specific energy than most available primary and rechargeable batteries. However, their energy density is limited by the deposition of lithium peroxide (a product of the air electrode reaction) within the pores of the air electrode, which interrupts the flow of current thereby limiting the usefulness of the device. Accordingly, recent research has focused on increasing the energy density of lithium–air batteries by using carbon gel with an appropriate tailored porous structure. The mesoporosity of carbon gels

accommodates a large volume of reaction products per gram of carbon and provides a catalytic surface for the Li/O_2 reaction. In addition, the pore structure is able to accommodate various bifunctional catalysts, while maintaining the desired mesoporosity. Thus, electrodes prepared from carbon gels comprise a high specific energy and resist the clogging and inactivation of the pores. Accordingly, it is reported that metal–air batteries have a greater energy density and active life when carbon gels are used, compared to devices prepared with other already commercialized carbon materials [8].

Fuel cells are direct energy conversion devices, which are being developed for numerous uses including electric vehicles, space power, remote power source, etc. [54]. Fuel cells typically use carbon composite electrodes, impregnated with platinum, rhodium or other noble metals. However, these electrodes suffer from high polarization resistance, resulting in a limited power capability [54]. The problem associated with high polarization resistance is largely due to the rate-limiting catalysis of the oxygen reduction reaction, which is proportional to the surface area of the electrodes. It is clear therefore that there is a need to provide electrodes with a high surface area so that they can be synthesized at an industrial scale. For this purpose, carbon gels are seen as potential material to prepare electrodes for fuel cells, since such materials not only have high surface area but an excellent electrical conductivity and controllable porosity [54]. Besides, carbon gel can be synthesized in several forms and from different precursor solutions, which could lead to the preparation of carbon-doped. Both features are of great relevance. On the one hand, carbon gel synthesized in the form of monoliths could be used to great advantage in fuel cell electrodes due to their higher electronic connectivity compared to powder, which reduces contact resistance. Furthermore, monolithic material also simplifies the fabrication of fuel cell assemblies since no binder is needed to prepare the electrodes [44]. On the other hand, as already mentioned throughout this chapter, carbon gel can be doped with nanotubes [31] or functionalized with sulphur to improve its catalytic activity in fuel cells [44].

2.5.2 *Catalyst Support*

Carbon gels are also used as catalysts in various catalytic support processes. For this application it is essential to dope the carbon gel with metals (active phase), as previously described. In general, the carbonaceous material must have a high mesoporosity, preferably with wide pores to allow the incorporation of the metal and the adsorption–desorption of reactants and products. Surface area must also be raised to allow a better dispersion of the active phase. Furthermore, the modification of the surface chemistry, especially in relation to oxygen and nitrogen groups, could enhance both catalytic activity and the durability of the catalysts.

2.5.3 Gas Storage

Great progress has been made in the field of hydrogen fuel generated from renewable power. However, there is still a need to improve the materials used in these devices. Carbon gels have great potential in this application and, for this reason, have been patented as hydrogen storage materials. It has been shown that microporosity and doping carbon gels with metals such as titanium, manganese, nickel or cerium enhances hydrogen storage [43, 45, 55].

2.5.4 Coatings

The use of organic and carbon gels as coating material has recently aroused a great deal of interest due to the stabilization and inertness of these materials under solidification conditions. Several patents can be found for this application, particularly in relation to thermal and acoustic insulating systems [56, 57]. The processes involve the application of the precursor solution to a surface of an object by spraying, screening, trowelling, slot die coating, cast coating, extrusion or a combination thereof to form the coating. These coating techniques are already applied at an industrial scale and allow several working cycles so that the thickness of the layer can be adapted to the requirements of the application of the coated surface, such as thermal and acoustic insulator systems or to meet the contours of aircraft and vehicles shapes [56, 57]. Furthermore, precursor solutions can be doped with fibres or inorganic compounds to improve the flexibility and mechanical properties of the coatings [56, 57].

Different types of coating can be applied to the surface depending on the final application. For example metal wires used in solid phase microextraction systems have been coated with a precursor solution of carbon gels. The devices obtained are robust, stable in fields of high radiation, and highly effective for collecting gas and liquid samples while maintaining superior mechanical and thermal stability during their routine use [58]. Furthermore, the time required for the extraction can be improved since a highly porous material allows a quicker uptake of analyte. Besides these applications, another interesting example is worth mentioning, i.e. organic gels which have been patented as molding materials [59]. The patented process consists in wetting a wax mold with the precursor solution and then converting the sol to a gel at a temperature below the softening point of the wax. The coated wax mold is then submitted to thermal treatment at a temperature above the pouring point of the wax in order to remove it. By this process, lightweight quasi-adiabatic molds with highly porous walls can be easily prepared.

Precursor solutions from which carbon gels are obtained have been also patented as impregnators for membranes such as cellulose [60, 61]. The impregnated membranes are then submitted to heat for the gelation and curing, then subjected to solvent exchange and drying after which they are finally carbonized.

A mechanically stable hydrophobic layer of carbon aerogel-cellulose membrane is obtained useful for use as active electrode material in fuel cells.

2.5.5 *Other Applications*

Apart from the patents already mentioned, there are other interesting cases to be highlighted. For example carbon gels have been patented as inner cushion materials for helmets to absorb the impact energy [62]. In general the porous structure of carbon gels requires the application of a large amount of energy to collapse. So that, upon impact the energy is used to collapse the structure and as a result the air inside the pores diffuse so quickly that they generate turbulences on a microscopic scale, converting the kinetic energy into heated air. Carbon gels have also been patented as filler filters for use in smokable products such as cigarettes [63]. Although this patent is quite striking, the incorporation of carbon gels into cigarette filters does not increase their capacity to absorb compounds such as nicotine, water or carbon monoxide. So this patent, although curious, does not seem to be of much commercial interest.

2.6 Conclusions

The aim of this chapter has been to provide the reader a general view of the current state of the art in the field of carbon gels production and uses. These synthetic carbonaceous materials have clearly great potential, due to the possibility to modify and design their properties according to each application. However, the number of patents in relation to the amount of research documents is still very low.

Most of the current patents deal with the improvement of some of their properties or their use in one of the numerous possible applications, but more effort to produce them at industrial scale in a cost effective process is needed. Very few of the current options of the synthesis process can be transferred effectively to the industry. Nevertheless, carbon gels have numerous potential applications with superior performance in comparison to the current materials used. Consequently, the synthesis option that achieves carbon gel production at industrial scale and at competitive prices will reach many different markets.

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