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Aerogels for energy and environmental applications

Aerogels are emerging as one of the most intriguing and promising groups of microporous materials, characterized by impressive properties such as low density, high surface area, high porosity and tunable surface chemistry. Fostering unique thermal and acoustic insulation features, for several decades they mainly received attention from the aerospace and building sectors. More recently, new great opportunities arose due to significant advances in the drying technologies that currently, represent the enabling step for aerogel synthesis and fabrication. This process-ability dramatically increased the interest toward aerogels from new disciplines. This explains why in the last decade the Environmental Science and Energy fields significantly contributed to the expansion of the aerogel technology, suggesting novel uses and applications and contributing to extend the group of materials that can be synthesized by aerogel processing. New, unforeseen properties emerged for aerogel materials, such as adsorption of contaminants and fluids purification, catalysis of different reactions, electrical conductivity. The present short-review aims at providing a critical overview of the key advances in the development of aerogels for energy and environmental applications, especially emphasizing the common strategies and properties that are turning aerogels into one of the new key emerging technologies of these areas of science.

Keywords: Aerogel, air cleaning, water remediation, energy production, energy storage.

Applicazioni ambientali ed energetiche degli aerogel. Gli ultimi avanzamenti nella ricerca dimostrano che gli aerogel sono una promettente classe di materiali microporosi grazie alle loro proprietà, come la bassa densità, l'elevata area superficiale, l'alta porosità e la loro chimica superficiale adatta a modifiche e funzionalizzazioni. Per decenni, gli aerogel sono stati ritenuti interessanti principalmente dai settori dell'aerospazio e dell'edilizia, grazie al continuo miglioramento delle loro proprietà isolanti in ambito sia termico sia acustico. Più recentemente, gli avanzamenti tecnologici riguardanti i processi di essiccazione, necessari per lo step finale di sintetizzazione dell'aerogel, hanno aperto la strada a nuove interessanti opportunità rendendo possibile l'accesso degli aerogel a nuovi ambiti di applicazione. In questo contesto, negli ultimi dieci anni, le scienze ambientali ed energetiche hanno contribuito in maniera significativa allo sviluppo della tecnologia in questione, proponendo nuove applicazioni e contribuendo all'ampiamiento delle classi di materiali che possono essere sintetizzati in forma di aerogel. Per nuove applicazioni si intende, per esempio, l'adsorbimento di contaminanti, il trattamento di fluidi e la catalisi. Inoltre, l'avanzamento tecnologico ha messo in luce nuove proprietà come, ad esempio, la conducibilità elettrica. L'obiettivo della seguente mini-review è di fornire una panoramica sugli avanzamenti nello sviluppo degli aerogel per applicazioni ambientali ed energetiche, specialmente enfatizzando le strategie comuni e le proprietà che hanno portato gli aerogel a essere una delle tecnologie chiave emergenti in queste aree della scienza.

Parole chiave: Aerogel, purificazione dell'aria, bonifica delle acque, produzione di energia, stoccaggio di energia.

1. Introduction

The International Union of Pure and Applied Chemistry (IUPAC) defines an aerogel material as "a gel comprised of a microporous solid in which the dispersed phase is a gas" (McNaught and Wilkinson, 1997).

Aerogels were firstly introduced by S. Kistler in the '30s, during experiments in which he extracted

the liquid filling the pores of wet gels (Kistler, 1931, 1932) obtaining solid silica-based materials whose pores, filled by air, showed dimensions close to those of the starting wet gel. Aerogel is actually a general term, referring to any material of any class (i.e., organic or inorganic, ceramic or semiconducting) in which a three-dimensional, highly-porous, continuous solid is

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obtained by an appropriate drying process applied to a wet gel.

At the time of their discovery, aerogel synthesis was quite challenging from a technical point of view and it is only during the last decades that they received a renewed attention especially due to advances in the available drying technologies (Aegerter *et al.*, 2011). Currently, synthesis routes are available for preparing almost all kind of materials in aerogel structure, including inorganic (such as SiO₂, ZrO₂, TiO₂, Al₂O₃, etc.) (Moner-Girona *et al.*, 2003; Baumann *et al.*, 2005; Aegerter *et al.*, 2011; Aegerter *et al.*, 2011), organic (i.e. polyurethane, resorcinol-formaldehyde (RF), polystyrene, polyimide, etc.) (Aegerter *et al.*, 2011), carbon-based and carbon-related materials (i.e. carbon, carbon nanotubes, graphene) (Horikawa *et al.*, 2004; Worsley *et al.* 2008; Wu, D., *et al.* 2012), semiconductor chalcogenide (i.e. PbTe, CdS, CdSe) (Aegerter *et al.*, 2011; Mohanan *et al.* 2005), natural based aerogels (i.e. polysaccharides, as agar and cellulose and proteins) (Aegerter *et al.*, 2011; Selmer *et al.* 2015; Betz *et al.* 2012) and recently, SiC-based aerogels (Kong *et al.* 2012; Kong *et al.*

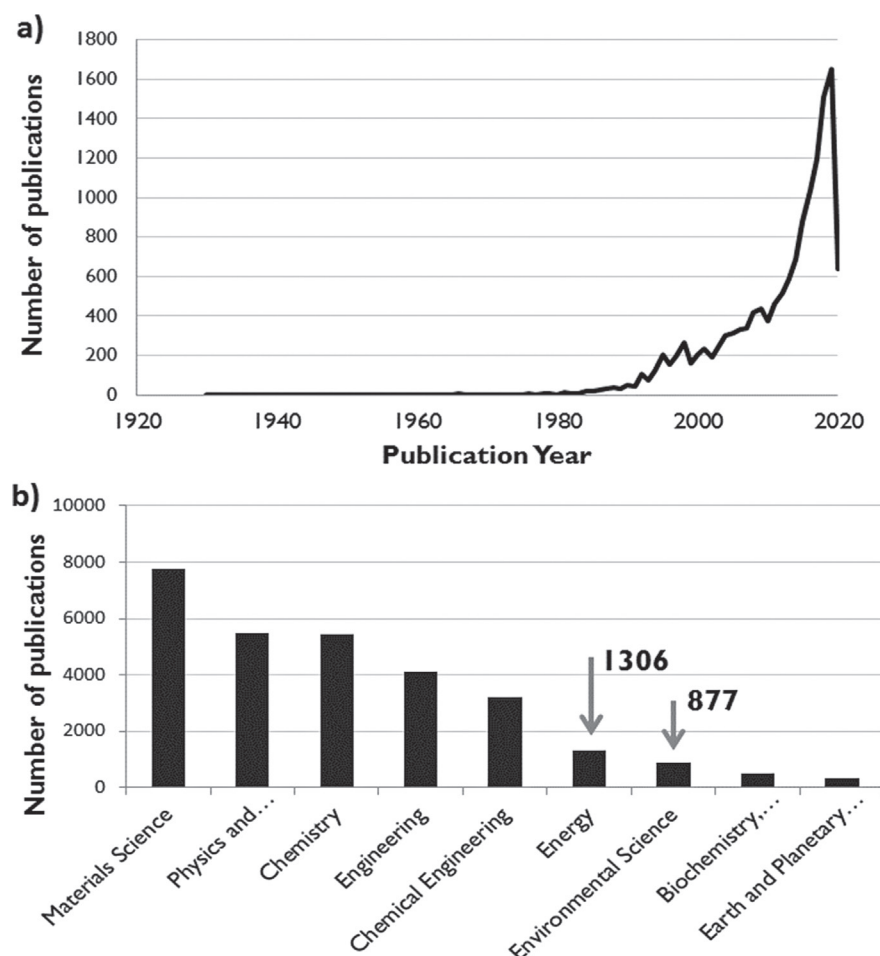


Fig. 1. a) Number of published articles per year, from 1930 to 2020, using the keyword "aerogel" for the search (April 2020, source: Scopus); b) Number of published articles for subject area: energy and environmental science are highlighted, they account for 1306 and 877 publications respectively.

a) Numero di articoli pubblicati per anno dal 1930 al 2020, utilizzando il termine "aerogel" come parola chiave per la ricerca (aprile 2020, fonte: Scopus); b) Numero di articoli pubblicati per area tematica: sono evidenziate le aree energia e scienze ambientali, che contribuiscono rispettivamente con un numero di pubblicazioni pari a 1306 e 877.

2013; Kong *et al.* 2014; Leventis *et al.* 2010; Worsley *et al.* 2010). Starting from the above mentioned single components different classes of composite aerogels were prepared, demonstrating the possibility to further improve the behavior of the materials to match the requirements for specific applications (Wang *et al.* 1995; Aegerter *et al.*, 2011; Ismail *et al.* 2004).

Traditionally aerogels attracted huge attention from the aerospace and building sectors because of their properties of thermal and acoustic insulation (Baetens *et al.* 2011; Randall *et al.* 2011; Ochoa *et al.*, 2012; Aegerter *et al.*, 2011).

The discovery of new aerogel synthesis and processing strategies for a wide range of materials allowed scientists to appreciate new and intriguing properties of the resulting nano- and micro-structured materials, useful for new applications. Indeed, from a general point of view, materials synthesized in the aerogel form combine a variety of morphologies and sizes with exclusive properties such as low density ($0.003\text{--}0.5\text{ g cm}^{-3}$), high surface area ($500\text{--}1200\text{ m}^2\text{ g}^{-1}$), high porosity (80–99.8%) and controlled surface chemistry, making these materials promising for a large number of applications (Maleki *et*

al., 2014), including, among many, catalysis (Maleki *et al.*, 2014), adsorption and environmental remediation (Matias *et al.* 2015; Perdigoto *et al.*, 2012; Reynolds *et al.*, 2001; Adebajo *et al.*, 2003), chemical sensing (Plata *et al.*, 2004), water remediation, energy production and storage (Mao *et al.*, 2018) and life science (Najberg *et al.*, 2020).

Environmental remediation and energy are two important fields of application for aerogels, as well demonstrated by Figure 1 in which the number of publications per year (retrieved using the keyword "aerogel" on Scopus) is analyzed since 1930, the year of their first demonstration. The curve in Figure 1a) clearly demonstrates an increasing interest towards aerogels during the last 20 years. A deeper analysis of the publications per subject area is proposed in Figure 1b), which allows one to appreciate the significant contributions from the energy and environmental science areas. From the first work on aerogels in 1931 a total of 14171 works have been published; out of these, 1306 publications refer to the energy sector and 877 to environmental science, the 95% of which in both areas have actually been published in the last 20 years. This impressive number is strictly related to the high performance that aerogels offer in these fields. Applications range from air cleaning, water remediation and CO₂ capture and conversion for Environmental Sciences to Energy Production, Storage and Distribution. Despite for the importance aerogels are gaining, only a few reviews focusing on aerogels analyzed from the perspectives of energy and environmental-related applications are currently available (Pajonk, 1991; Ulker *et al.*, 2014; Chen *et al.*, 2014; Maleki, 2016). However, none of them tries to analyze simultaneously the fundamental results obtained by the scientific community in these two

scientific fields. The present paper aims at providing a critical overview of the key advances in the development of aerogels for both energy and environmental applications, especially emphasizing the common strategies and properties that are turning aerogels into one of the key emerging technologies in these areas of science.

2. Aerogel synthesis

Aerogel synthesis is based on 3 phases: the sol-gel process, ageing, drying process.

The *sol-gel process* includes the colloidal dispersion of the precursors in liquid solution and the reactions that lead to the formation of a 3D network (gel). Gels are synthesized by hydrolysis and condensation of metals or semimetals in case of inorganic aerogel and by polymerization in case of organic aerogels (Pierre and Pajonk, 2002; Hüsing and Schubert, 1998). The *ageing* makes the gel network more

stable and avoids excessive shrinkage during the drying step (Soleimani Dorcheh and Abbasi, 2008); the gel is immersed in the solvent that will be removed during the drying step. During the *drying process* the liquid part is replaced by air and the aerogel is obtained. There are 3 possible *drying processes*: supercritical drying, freeze drying and evaporative drying (Vareda *et al.*, 2018). In the *supercritical process* there are two possible approaches: (1) the solvent inside the aerogel reaches the supercritical state and then the supercritical fluid is vented out, (2) supercritical CO₂ is used to extract the solvent and, in this case, the solvent must be soluble in supercritical CO₂ (Vareda *et al.*, 2018). In the *freeze drying process*, at first, the solvent is frozen and then it is sublimated under vacuum (Rigacci *et al.*, 2004). In the *evaporative drying* the solvent is simply evaporated at ambient pressure (Schwan and Ratke, 2013). In Figure 2 we represent the 3 different approaches in a schematic phase diagram.

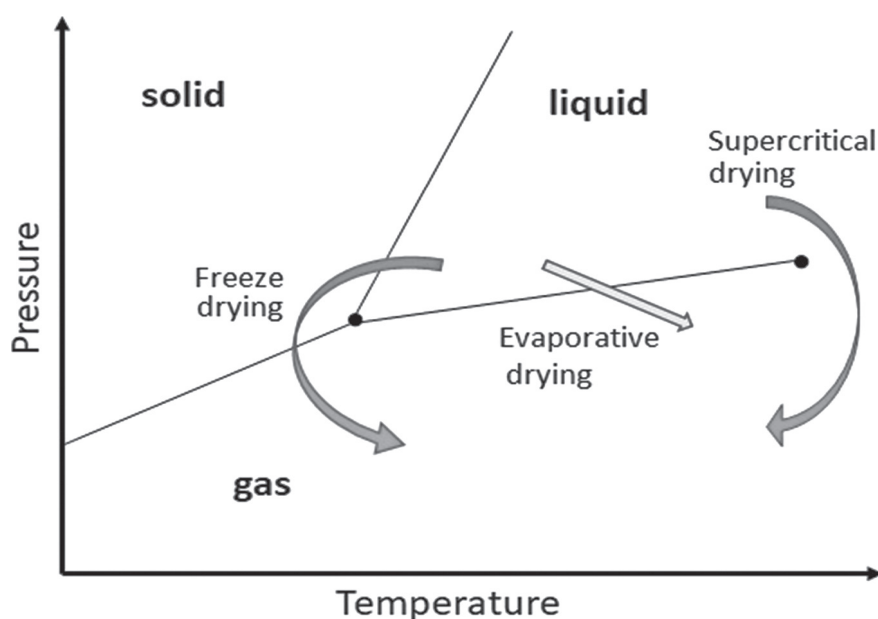


Fig. 2. Phase diagram scheme representing the 3 different drying process for aerogel: supercritical drying, freeze drying and evaporative drying.

Rappresentazione schematica di diagramma di fase che mostra le tre diverse modalità di asciugatura utilizzabili per la sintesi degli aerogel: asciugatura superscritica, liofilizzazione ed evaporazione.

2.1. Inorganic aerogels

Kistler synthesized a big variety of aerogels: besides silica based aerogels, he synthesized aerogels based on inorganic precursor as alumina, tungstic oxide, ferric oxide, stannic oxide, nickel tartrate and, also, organic precursor as cellulose, nitrocellulose, gelatin, agar, egg albumin and rubber (Kistler, 1932).

Silica aerogel (SiO₂) is the most studied material in inorganic chemistry field: it is obtained by the polymerization of silica precursors, for example sodium silicate (Na₂SiO₃) (Kistler, 1932) and the synthesized gel is characterized by a nanostructured 3D network with molecular chains of Silicon (Si) and Carbon (C) linked by covalent bond (Hüsing and Schubert, 1998). The Silica aerogel has a transparent appearance and it is characterized by: an extreme porosity (about 90%), with pores having diameters in the range 20-40 nm, a density less than 0.05 g/cm³ that, in some cases, could reach 0.003 g/cm³, a high specific surface area in the range of 250-1000 m²/g (Hüsing and Schubert, 1998). All the properties are linked to the sol-gel phase, drying and post-drying processes. Silica aerogels are very good insulating materials for two main reasons: first, the pores structure makes them a convective inhibitor because air cannot circulate through the network and, secondly, the silica itself is a poorly conductive material as dense silica glass and silica powder have a conductivity about 1 and 0.025 W/mK respectively (Yoldas *et al.*, 2000). The conductivity of silica aerogels is between 0.0154 and 0.0053 W/mK, depending on the pores size (Yoldas *et al.*, 2000) and is lower than air conductivity in the same conditions (0.025 W/mK) (Aegerter *et al.*, 2011). For the same reasons, these aerogels are acoustic insulating materials (Cotana *et al.*, 2014): the acoustic

propagation is difficult inside the nanostructure and the mechanism is similar to thermal conductivity. The mechanical performances are not extraordinary, they are brittle materials: for a silica aerogel with density of 0.112 g/cm^3 , the resistance to compression is $1.8 \times 10^4 \text{ Pa}$ (Deng *et al.*, 1998). Mechanical behavior depends on synthesis process and precursors and they could be different (Aegerter *et al.*, 2011); anyway this kind of aerogel are characterized by brittleness and their possible applications are limited (Deng *et al.*, 1998).

Besides silica aerogel, other inorganic aerogels were studied: non-silicate inorganic aerogels could be easily synthesized from metal oxide precursors (Hüsing and Schubert, 1998).

Zirconia aerogel (ZrO_2) is a very interesting material and could be used as catalyst or catalyst support thanks to its high surface area (Ward *et al.*, 1993; Bedilo *et al.*, 1998). Generally, Zirconia aerogels have a density of $0.2\text{-}0.3 \text{ g/cm}^3$, porosity between 84-96%, pore radii of 10 nm and a surface area of $81\text{-}480 \text{ m}^2/\text{g}$ (Hüsing and Schubert, 1998). Zirconia surface is known for its chemical properties: it is characterized by acid and basic sites in which reduction and oxidation are possible (Ferino *et al.*, 2000). Thanks to its electrical, thermal and mechanical properties, Zirconia is widely applied in the ceramic industry as a component for fuel cells, coatings, oxygen sensors and high temperature component applications (Aegerter *et al.*, 2011). Zirconia aerogels have slightly better mechanical behavior than Silica aerogels: within the same density range, the Young modulus of Zirconia aerogel is 10.7 MPa while the Silica aerogel value is $2\text{-}3 \text{ MPa}$ (Benad *et al.*, 2018).

Alumina aerogels (AlO_2) are another class of interesting aerogels for their relatively high strength, thermal and chemical

stability at high temperatures (Zu *et al.*, 2011). Compared to silica aerogels alumina aerogels have better thermal insulation properties at high temperatures thus they are a promising candidate for high-temperature applications (thermal superinsulations, heat-storage systems, catalysts) (Zu *et al.*, 2011). Aerogels based on Alumina are largely used as catalytic supports because of their resistance at high temperature and high surface area (Mizushima and Hori, 1994). Anyway, it is difficult to synthesize a pure monolithic Alumina aerogel without fractures and that remains stable in humid conditions (Poco *et al.*, 2001).

2.2. Organic and carbon-based aerogels

In this group we consider all the aerogels whose chemistry is characterized by organic compounds as natural and synthetic polymers. Organic compounds are characterized by strong Carbon-Carbon covalent bonds that make the synthesis of macroscale monolithic aerogels possible. These materials are innovative because they can tolerate high mechanical stress both under compression and bending forces (Diascorn *et al.*, 2015). In general, organic aerogels are synthesized by polycondensation. In order to obtain the gels, it is necessary that precursor monomers contain more than 2 functional groups: with only 2 reactive groups the final polymer will be linear but, to achieve the gel condition (from the sol to the gel step), at least 3 functional groups should react in order to create a crosslinked 3D nanostructure. This kind of polymers are classified as thermosets, their chemistry is irreversible and they cannot be melted because with the increasing of temperature they degrade. In general, organic aerogels are non-transparent and

less brittle than inorganic aerogels (Aegerter *et al.*, 2011). The most studied aerogels are based on Resorcinol-Formaldehyde, Polyimide and Polyurethane (Aegerter *et al.*, 2011; Rigacci *et al.*, 2004).

In 1989, Pekala was the first to synthesize polymer-based aerogels through the polycondensation of Resorcinol with Formaldehyde (RF) (Pekala, 1989). In RF chemistry, the functional groups are the hydroxylic group (OH) and the carbonyl group (C=O). RF aerogels have high porosity ($>80\%$), with pores having diameter less than 500 Å , a surface area between $400\text{-}900 \text{ m}^2/\text{g}$ and a density of 0.03 g/cm^3 (Pekala and Schaefer, 1993). Aerogels based on resorcinol-formaldehyde are very interesting materials with applications in thermal insulation, catalysis (Aegerter *et al.*, 2011) and as precursors of Carbon-based aerogels whose description was made only at a later time. A study by Yang *et al.* (2010) reports the synthesis of a RF aerogel that has an energy absorption per unit volume higher than an Aluminum foam characterized by similar density: this could open a new application path for RF aerogel as a material for protection under an impact. It should be noted that Formaldehyde is classified by IARC (International Agency for Research on Cancer) as *carcinogenic to humans* and, for this reason, it is losing its appeal for new possible studies and applications.

More recent studies are focused on Polyurethanes aerogels (Biesmans *et al.*, 1998; Tabor, 1995; Pirard *et al.*, 2003; Rigacci *et al.*, 2004; Diascorn *et al.*, 2015). Polyurethanes include a large variety of polymers whose chemistry is characterized by organic units joined by carbamate (urethane) link. The synthesis involves an isocyanate that contains 2 or more functional groups and a polyol with 2 or more hydroxylic groups. The main application is thermal insulation

(Rigacci *et al.*, 2004; Diascorn *et al.*, 2015) but, because of their variety, linked to the chosen polyols and isocyanate, a lot of possible applications could be explored. In Table 1, we compare the properties of different synthesized Polyurethane aerogels.

It is possible to note that all the Polyurethane aerogels have low density, low thermal conductivity and high surface area. Moreover, the study by Diascorn *et al.* (2015) reports of an aerogel with a compressive modulus of 7.8 MPa which can tolerate high strains without breaking. They could be a valid alternative to RF and Silica aerogels.

Organic aerogels based on natural polymers are very interesting because they meet the current demand of more sustainable chemical compounds. Cellulose is the most abundant polymer in nature: it can be synthesized from plants or from some bacteria (Brigham, 2018). It is a polysaccharide characterized by linear chains composed by $\beta(1 \rightarrow 4)$ linked D-glucose units. The degree of polymerization depends on the origin of the raw material: generally, cellulose from wood pulp contains 6000- 10000 units and cellulose from cotton contains 10000- 15000 units (Aegerter *et al.*, 2011). A huge variety of cellulose is available and it is difficult to provide raw material with the same chemical characteristics. This could be a problem for applications which should guarantee a specific product with constant performances over time.

Cellulose aerogels are white and

non-transparent, they have a surface area about 300 m²/g (when they are obtained by supercritical drying) and density in the range of 100-350 kg/m³ (Hoepfner *et al.*, 2008). One of the first works about cellulose (Tan *et al.*, 2001) showed how it was possible to create a cross-linked cellulose aerogel with high-impact strain; the authors suggested possible applications under rugged conditions as coating, thermal insulator, acoustic barrier and membrane.

Carbon aerogels are interesting materials with possible innovative applications in catalysis, adsorption and energy storage (Worsley *et al.*, 2010). Pekala was the first to synthesize carbon aerogels (Pekala, 1991) by the pyrolysis of Resorcinol-Formaldehyde aerogel: the material is thermally decomposed at elevated temperatures in inert atmosphere. Lately, other researchers worked at optimizing the properties of Carbon aerogel for specific applications: for example, enhancement of the electrical, thermal and mechanical properties: Some works discuss the addition of additives during the sol-gel step, such as carbon nanotubes or graphene sheets (Worsley *et al.*, 2010; Tao *et al.*, 2007; Bordjiba *et al.*, 2007). Another work shows the possibility of precursors functionalization to introduce a specific functional group into the carbon aerogel final network (Baker *et al.*, 2004). Generally, Carbon aerogels have uniform mesopores that depend on the agglomerate structures of uniform spherical carbon

particles (Yao *et al.*, 2010) and they offer the advantage of a tunable three dimensional hierarchical morphology compared to other porous carbon materials (Biener *et al.*, 2011). In one study (Hwang and Hyun, 2004) the synthesis of a Carbon aerogel as electrode, obtained by pyrolyzing of RF aerogels, with high specific surface area (400-700 m²/g), low density (0.40-1.16 g/cm³) and ultrafine pore size (<50 nm) is reported. In another publication (Pekala *et al.*, 1998) Carbon aerogel for electrochemical applications with similar data (surface area 400-800 m²/g and pore size <100 nm) is presented. All the characteristics of Carbon aerogels and, in particular, their enhanced electrical properties carry a technological promise for a variety of sustainable energy applications.

3. Environmental applications

In energy applications, for both storage and conversion, carbon-based materials play a crucial to prepare efficient electrodes and carbon-based aerogels offer incredible opportunities to tune the porosity and surface chemistry while ensuring electrical conductivity.

3.1. Air cleaning

The increasing concerns about the effects of emissions and volatile hazardous compounds on

Tab. 1. Main properties of Polyurethane aerogels reported by the main reference articles.
Principali proprietà degli aerogel in poliuretano secondo i dati riportati nelle principali pubblicazioni.

Authors	Tabor, 1995	Biesmans <i>et al.</i> , 1998	Biesmans, 1999	Biesmans <i>et al.</i> , 2000	Diascorn <i>et al.</i> , 2015
Drying process	evaporation	supercritical CO ₂	supercritical CO ₂	evaporation	supercritical CO ₂
Density [g/cm ³]	0.15-0.50	0.10-0.25	0.05-0.15	0.1-0.3	0.23-0.12
Pores dimension [nm]	-	14±3	-	-	15-70
Surface area [m ² /g]	-	570±30	-	50	100-200
Thermal conductivity [W/m K]	0.033	0.016±0.001	0.018	29	-

human health and on the environment have triggered investigations on several classes of phenomena, leading to a better knowledge and significantly boosting scientific and technological innovation. Volatile Organic Compounds (VOCs) are among the most common air pollutants released into the atmosphere from industrial activities associated to chemical, petrochemical and related sectors (Zhu *et al.*, 2020). They are a group of organic substances characterized by a low boiling point (Wang *et al.*, 2007). Benzene, toluene, ethylbenzene and xylene, also known as BTEX are the most commonly emitted VOCs and they are all recognized as highly toxic and carcinogenic. Thus effective methods to remove them from flue gas are needed. Abatement methods can be classified in two main groups: destruction technologies, that imply the decomposition of VOCs into carbon dioxide and water by chemical or biological approaches; and, recovery technologies, that aim at separating VOCs from the gaseous phase via physical processes. Adsorption is the most common way to recover these volatile compounds vapor from the atmosphere (Li *et al.*, 2020). In this framework aerogels, with their micro- and even meso-porous structure, high surface area and tunable pore surface properties and chemistry, are emerging as efficient adsorbents (Fairen-Jimenez *et al.*, 2007).

The possibility of adsorbing toluene vapors was demonstrated with activated carbon aerogels, reaching a maximum capacity of 1180 mg/g and also showing excellent results in terms of material regeneration, with a complete desorption at 400 °C (Dingcai *et al.*, 2006; Maldonado-Hodar *et al.*, 2007). Benzene vapors were effectively captured by silica aerogels, which are establishing as a promising sorbent with a capacity as high as 3000 mg/g; this result is

impressive especially if compared to the behavior of standard activated carbon powders, which have a capacity of 500 mg/g (Jun *et al.*, 2008).

Moreover, silica aerogels were successfully modified for BTEX vapors removal directly from gas streams (Standeker *et al.*, 2009). Surface modification by methyltrimethoxysilane (MTMS) and trimethylethoxysilane (TMES) have been used for this purpose, also improving aerogels reusability.

Another important source of air contamination is anthropic emission of carbon dioxide, which is the main responsible for climate change. Tackling this environmental challenge requires not only to reduce CO₂ emissions but also to capture the CO₂ already emitted from air and flue gas. Technological approaches for CO₂ capture must be economically sustainable for large-scale applications. Porous solid materials such as zeolites, metal organic frameworks (MOFs), activated carbon and calcium oxides, etc. are emerging as key technologies for this purpose (Choi *et al.*, 2009; Radosz *et al.*, 2008; Gil *et al.*, 2015).

Aerogels are demonstrating to offer the right set of tunable properties to take part to this environmental challenge, especially being designed and synthesized as the support for chemical groups, as amines, that can actively capture CO₂. This approach is demonstrating to be particularly effective since aerogels offer high degrees of freedom to tailor their microporous structure, composition and surface chemistry to specifically address CO₂ capturing purposes (Rechberger *et al.*, 2014; Pierre and Pajonk, 2002). Good examples of this approach are amine modified silica aerogels. Both 3-aminopropyltriethoxysilane (APTES) (Cui *et al.*, 2011) and tetraethylenepentamine (TEPA) (Qi *et al.*, 2011) were successfully

investigated for CO₂ adsorption, reaching the impressive capacity of 6.97 mmol/g and 7.9 mmol/g in simulated flue gas conditions (with 10% CO₂), respectively (Lineen *et al.*, 2013).

3.2. Water treatment

Clean water is an essential resource for life and for many human-related activities. Therefore, preserving water quality by sustainable and effective methods is one of the key challenges faced at the global scale. Industries and municipalities are the main sources of toxic substances seriously compromising water quality and water-based ecosystems. Two main groups of toxicants can be considered, i.e. organic contaminants and heavy ions. In both cases the properties of aerogels in terms of low density, tunable chemistry and high surface area make them the ideal candidates for applications in water remediation (Standeker *et al.*, 2007).

Organic contaminants that can be found in water and impacting on aquatic environments include herbicides, pesticides, plant and animal fats, heavy and light hydrocarbons (Yang *et al.*, 2013). Physical, chemical and biological methods were developed to tackle water remediation (Ayotamuno *et al.*, 2006) and among them physical treatments, mainly adsorption, are the most effective to remove organic toxicants from water (Zhang *et al.*, 2012; Zhang *et al.*, 2014).

Silica aerogels with tunable surface hydrophobicity were successfully developed to adsorb both miscible and immiscible organics (Standeker *et al.*, 2007). Since sustainability of adsorbents is an essential requirement for this class of applications, cellulose aerogels are an important emerging group of materials (Cai *et al.*, 2008). They indeed combine adsorbing capaci-

ty, as high as 20 g/g (Korhonen *et al.*, 2011), to green chemistry approaches as they are synthesized by combining the use of tarting raw cellulose fibers derived from different natural sources (Moon *et al.*, 2011) to the use of recycled paper wastes (Nguyen *et al.*, 2013). Another important class of aerogel materials that attracted particular attention over the last years are carbon aerogels that combine a highly porous three-dimensional (3D) structure with surface hydrophobicity, thus featuring as excellent oil adsorption media (Zhang *et al.*, 2013). Moreover, environmentally sustainable and cost-effective carbon aerogels can be obtained from biomass sources (Li *et al.*, 2014).

Heavy ions are another important source of environmental pollution, mainly originated from industrial discharges. Many of them (e.g. chromium, lead, mercury, cadmium, nickel) are known to be highly toxic with detrimental effects on the environment and human health (Amoyaw and Bu, 2009). In this field too, among the different possible approaches, adsorption methods are considered effective and reliable for large-scale applications and active carbons are the most frequently proposed materials (Anirudhan and Sreekumari, 2011).

The properties of aerogels as adsorbents are emerging also for this application, especially showing again the huge advantages that they can offer in terms of tuned porosity and surface chemistry to meet the specific requirements of the final application. An effective strategy to capture heavy metal ions is to introduce functional groups containing N, O, S and donor atoms, able to form coordination complexes with metal ions (Kudryavtsev *et al.*, 1990). Following this approach, several aerogel materials were developed such as heavy metal ions adsorbents.

Amino modified silica aerogels demonstrated good chemisorption of Cu (II) ions (Soliman, 1997), while amino modified resorcinol-formaldehyde aerogels were used to capture Pb(II), Hg(II) and Cd(II) ions from aqueous solution; and maximum sorption capacities of 156.25, 158.73 and 151.52 mg/g were observed, respectively (Motahari *et al.*, 2015). A Carbon aerogel obtained by pyrolytic carbonization of RF aerogels was also proposed that showed an impressive adsorption capacity for Cd(II) of 400.8 mg/g (Kumar *et al.*, 2005).

4. Energy related application

In energy applications, both for storage and conversion, carbon-based materials play a crucial role to prepare efficient electrodes and carbon-based aerogels offer incredible opportunities to tune the porosity and surface chemistry while ensuring electrical conductivity.

Contribution of renewable energy sources (wind, wave and solar) is expected to continue growing over the next decade, this makes urgent the need for efficient and robust energy storage technologies that can help mitigating the effects of the inherent intermittency of renewables. Electrochemical energy storage through batteries, especially lithium ion batteries and supercapacitors has established during the last decades as the best technological choices to address this issue. In lithium ion batteries a negative and a positive electrodes are present, separated by a non-aqueous lithium-ion conducting electrolyte. Both the electrodes are able to reversibly intercalate Li⁺ ions. During discharge, Li⁺ ions carry the current from the negative to the positive electrode, through the non-aqueous electrolyte. During charge,

an external high voltage is applied that forces lithium ions to migrate from the positive to the negative electrode, where intercalation occurs (Bianco *et al.*, 2016).

Supercapacitors are energy storage devices able to store charges in the electrical double layer of carbon-material with high-surface area. The storage mechanism is a physical one, based on the separation of positive and negative charges. Therefore, supercapacitors represent an intermediate device between batteries and electrostatic capacitors (Pekala *et al.*, 1998; Conway, 1991). The energy density of supercapacitors is lower than for batteries but higher than that of an electrostatic capacitor; for power density the opposite is true. Given these operative differences, supercapacitors are the ideal complement to batteries to deal with peak power demand.

For both supercapacitors and batteries, the advent of carbon-based aerogels, especially in the form of graphene-based aerogel, significantly contributed to the improvement of their storing capacities by new aerogel based electrodes (Mao *et al.*, 2018). In lithium ion batteries the use of carbon-based – and particularly graphene-based aerogels – is especially related to the possibility of reducing the mechanical strain of the electrodes due to the insertion/removal of Li ions during cycling. This is achieved by exploiting all the advantages offered by the tunable size of pores into the resulting electrodes, by modifying their surface chemistry (even by decoration with other nanomaterials) and eventually to design them as composites (Hu *et al.*, 2016; Yang *et al.*, 2013; Wu *et al.*, 2011; Zhu *et al.*, 2011).

In supercapacitors the key goals for device optimization are related to increasing both energy and power densities as well as the operating voltage together with decreasing the cost per Wh stored in the

device. Optimization of advanced electrode materials is the route to improve these properties (Gamby *et al.*, 2001; Robinson 2010). Carbon aerogels are the ideal materials for this purpose as they combine chemical inertness to high conductivity and by the use of proper raw materials they can be made environmentally friendly and cheap. The performance of carbon aerogel-based electrodes is optimized thanks to the possibility aerogels offer, to improve energy and power densities because of their high porosity. Moreover, the porous structure of carbon aerogels can be tuned in a hierarchical structure, combining both macropores, for good mass transport which is related to power density and micropores, to provide the high surface area necessary for high energy density (Wu *et al.*, 2012).

Among the devices for energy conversion, fuel cells (FCs), especially proton exchange membrane FCs (PEMFCs) are gaining increasing importance as a clean and sustainable energy source. What still hinders the market ability of PEMFCs is the limited efficiency of the Oxygen Reduction Reaction (ORR) occurring at the cathode of these systems. PEMFCs are electrochemical devices that convert the chemical energy of different classes of molecules (i.e. the fuels, such as H_2 , methanol, ethanol) into electricity when proper catalysts are present. Over the last years, the use of nanomaterials significantly improved performance and reliability of fuel cells while contributing to lower their costs (Zhang *et al.*, 2015). However, efforts are still needed to make the cost of the devices competitive. The bottleneck is precisely the ORR because oxygen is supposed to react with both electrons and protons to form H_2O (4 electrons absorbed). If the catalyst is not efficient enough H_2O_2 is produced, limiting the efficiency of device

and compromising its stability over time. This reaction not only occurs at the cathode of the fuel cells but also characterizes metal-air batteries. Platinum and related materials are recognized as the best catalyst for ORR but costs and scarcity are pushing the scientific community to identify adequate substitutes (Li, 2019). In the perspective to design new, effective electrodes able to properly catalyze the ORR, carbon based aerogels offer great opportunities to couple electrical conductivity, high surface area and easily controllable surface chemistry (Shaari and Kamarudin, 2019).

5. Conclusions

Aerogels are extraordinary materials, with a unique set of properties that make them interesting for several application fields. High surface area, high porosity and ease of surface chemistry modification have especially attracted attention from the energy and environmental science. In this review we especially showed that impressive results have been obtained during the last decades thanks to advances in aerogel technology and those improvements are directly reflected in the large number of materials that are now available in aerogel form. Energy and Environmental Science significantly contributed to the improvement of aerogels, especially helping to appreciate to which extent aerogels properties can be tuned towards the need of different applications, especially in terms of their adsorption, catalytic behavior and electrical conductivity.

The possibility to tune their physical and chemical properties, combined with the flexibility of their synthesis process, make aerogels key candidates for environmental protection and remediation. In the

present review impressive examples have been analyzed, that show how versatile aerogels are to design efficient absorbents for VOCs, CO_2 , as well as useful instruments for water remediation, especially for oil and heavy metal ions segregation.

At the same time their properties can be tuned to synthesize successful and enabling materials for energy applications. In this field aerogels are contributing to the design and optimization of the new generation of electrodes for energy storage devices, especially in supercapacitors and batteries and for energy conversion, such as in fuel cells.

Due to their exceptional potential, aerogels are now establishing as essential contributors for future progress of these scientific areas.

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