



71st Conference of the Italian Thermal Machines Engineering Association, ATI2016, 14-16  
September 2016, Turin, Italy

## Nanodevices and novel materials for energy-efficient constructions

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### Abstract

The development of novel technologies exploiting the astonishing properties of nanomaterials is quickly advancing. Among the plethora of available innovative materials and devices, we selected aerogel, phase change materials and two specific classes of chromogenic devices, namely electrochromics and photoelectrochromics. The recent outcomes from these widely investigated fields highlight very interesting opportunities in the design of smart, multifunctional building envelopes. A critical overview of these fields of investigation is provided hereafter, with particular attention towards applications, costs and potential energy-savings.

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Peer-review under responsibility of the Scientific Committee of ATI 2016.

*Keywords:* Aerogel; Phase change materials; Chromogenic devices.

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### 1. Introduction

The progressive depletion of fossil energy resources and the growing attention devoted to environmental issues, such as global warming and climate change, call for innovative and non-polluting technologies devoted to energy saving and renewable energy exploitation. There is a strong interest towards innovative materials and novel energy technologies, capable of mitigating the energy consumption in the construction sector, reaching 40% share almost worldwide [1]. Such materials and devices, especially deriving from the huge research effort in the cross-disciplinary field of nanotechnology, show several advantages: reduction of raw materials involved in processes, lower amount of energy used in production, higher level of customization for structure, morphology and features. For these and other reasons, they are often named “enabling technologies”, spanning from “bioinspired” nano-coatings to novel devices

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[2,3]. This paper reviews the state of the art in some available technologies, pointing out their pros and cons, with particular reference to aerogel, PCMs, chromogenic devices, particularly relevant with respect to the enhancement of performances in building envelopes. Among different available technologies, silica aerogels are gels dried in “supercritical” conditions, showing low weight, very high thermal insulation properties (0.014 W/(m K)), elevated porosity (80–99.8%), low density [4]. Despite these dramatic figures of merit, they are still too expensive to allow a wide exploitation in the building industry both in the opaque and in the translucent form. PCMs [5] have attracted wide attention. They are capable of absorbing, storing and releasing a large amount of heat at given, constant temperatures. Dynamic tintable glazings (electrochromic and photoelectrochromic devices) [6,7] are very promising technologies, allowing variable energy throughputs in windows, which are normally considered as thermal weak points in constructions but during the hot season, may conversely cause excessive solar loads that require HVAC systems, with an increase in energy consumptions. Then, controlling the transmitted energy fraction may contribute significantly to energy savings in buildings. The aim of this review paper is to show the opportunities coming from innovative technologies in terms of energy savings applied to both new and existing buildings. In particular, most of the investigated technologies could be suitable for refurbishments and energy retrofitting, also in historical and cultural heritage buildings. In fact, as reported by Ascione et al. [8] new buildings are only 1% of the total European stock, while significant renovations regard about the 1.8% of the existing buildings.

### Nomenclature

$\lambda$	thermal conductivity (W/(m·K))	UDI	Useful Daylight Illuminance
PCM	Phase change material	PEC	photoelectrochromic
EC	Electrochromic	PVC	Photovoltachromic

## 2. Novel technologies for building envelopes

### 2.1. Aerogel superinsulation

Aerogel is a porous material. Its preparation is based on sol-gel technique [9], a method allowing the production of solid materials from small molecules. Silica sol-gels are formed via hydrolysis and polycondensation reactions of silica precursors, mainly tetraethyl orthosilicate (TEOS), tetramethylorthosilicate (TMOS), or polyethoxydisiloxane, in the presence of acid or base catalysts [10]. The sol becomes a gel when the solid nanoparticles distributed into it stick together to form a medium of particles spanning the liquid [11].

A simplified reaction for silica aerogel, with TEOS as an alkoxide precursor is reported in (1):



Afterwards, two more steps are required in order to obtain aerogel: aging and drying. The former is required to rise the degree of cross-linking and to provide sufficient time to strengthen the silica network, if necessary by adding new monomers to the SiO network. At the end of aging, all water in the pores must be removed, by washing the gel with ethanol or heptanes [12]. In fact, residual water would result in opaque or very dense aerogel.

The drying phase, a capillary pressure controlled process, generally takes place in supercritical conditions, allowing the removal of the pore liquid above the critical temperature and pressure of the solvent. At this stage, there is no liquid-vapour interface and no capillary tension, which could lead to mechanical damage, shrinkage, cracking and structural collapse. An overall  $\lambda$  of 13.5 mW/(m·K) at ambient pressure (or 4 mW/(m·K) at a pressure of 50 mbar) has been reported for silica aerogel. State-of-the-art commercially available aerogel for building insulation has reached  $\lambda$  between 13.1 and 13.6 mW/(m·K) at ambient temperature (up to a temperature of 200°C). An interesting classification of aerogel superinsulation materials was provided by Koebel et al. [13]. They also reported some considerations about the global market share of “other insulation” products, accounting for 1.1 billion USD (already in 2008). Aerogel insulation panels 7.5 cm thick ( $\lambda=0.015$  W/(m·K)) show the same performance of 16 cm thick conventional insulation

( $\lambda=0.032 \text{ W}/(\text{m}\cdot\text{K})$ ). A significant space saving can be obtained, at the expense of a dramatic increase of materials cost, passing from 15 USD/m<sup>2</sup> for conventional insulators to 280 USD for aerogels. For monolithic aerogel to be included in windows, the authors estimated an additional cost of 100 USD per square meter, without taking into account the significantly higher price tag due to the more delicate handling and processing steps. Aerogel proved to be a strategic material in the challenge to increase thermal performances of opaque building envelopes and windows, as well as for attenuating the effects of thermal bridges. Aerogel can also act as an aggregate for lightweight and thermal insulating concrete, as reported in [14]. Duer et al. [15] studied the use of silica aerogel as an insulator in evacuated windows, reporting not only the significant thermal enhancement, especially relevant for heating dominated climates, but also the main concern for their application in glazing: scattering of monolithic aerogel, resulting in hazy pictures when objects were viewed through the material. More recently, Gao et al. [16] studied insulating glazing unit filled with silica aerogel granules. Their experimental results showed how the particle size affected the optical and thermal properties of glazing units. Small sized aerogel granules (size <0.5 mm) showed a 63% reduction in heat losses, with a solar factor of 0.27, whereas large-sized aerogels (3-5 mm) reported a 58% reduction with a solar factor of 0.57. The same research group [17] observed the enhancement of optical and mechanical features of transparent monolithic aerogel for glazings as a consequence of sintering aerogel precursors at elevated temperatures, obtaining a material with low thermal conductivity (0.17–0.18 W/(m·K)), high visible transparency (91–96 % at 500 nm), low density (1.60–1.79 g/cm<sup>3</sup>) and enhanced mechanical strength (2.0–6.4 GPa).

Ihara et al. [18] reported experimental results showing that aerogel granules can undergo an increase of ~10% in  $\lambda$  in environments with sustained fluctuations in humidity, consequent to silica-network breakage during aging. Therefore, appropriate maintenance may be required (installation specifications) to ensure the sustained thermal performance of aerogels. Berardi [19] illustrated how the use of aerogel may represent a manifold choice, reporting the results coming from different retrofitting strategies. Buratti et al. [20] reported the outcomes of simulations performed using both Energy Plus and TRNSYS, comparing different scenarios in terms of energy demand, such as the substitution of the glazing and the use of innovative package solutions. Results showed that an important energy saving was obtained for all the proposed glazings (about 60–70%). In a previous work [21], they demonstrated that aerogel is one of the most promising materials for use in highly energy-efficient windows, showing low  $\lambda$  (down to 0.010 W/(m·K) in evacuated conditions), a high solar energy and daylight transmittance was achieved. They also observed that monolithic aerogel introduced a better light transmittance (0.60) than the granular one (0.27) and that heat losses were reduced by 55%, if compared to a conventional window.

Cuce et al. [22] analysed, among the other things, the effect a 20 mm thick fibre–silica opaque aerogel blanket has on the internal side of a test bedroom, and measured the heat flux from the separating wall, comparing the cases of pre and post-retrofit, revealing the crucial influence of internal aerogel retrofitting on the heat loss due to the thermal bridges. Huang et al. [23] conducted an annual HVAC system energy analysis indicating that in humid subtropical climates the application of silica aerogel glazing system can reduce the annual space cooling load by around 3.5-4% in the hottest months, in a typical commercial building, with a reduction of 60% of the envelope heat load.

Ibrahim et al. [24] reported the effects of a recently patented silica-aerogel-based insulating coating on the thermal performances of exterior walls, in a French Mediterranean climate. Their numerical study demonstrated that the aerogel-based insulating coating showed better performance than other insulating materials due to both lower  $\lambda$  and higher thermal mass. They used the same insulating paint in order to limit the thermal bridge losses, demonstrating that, by applying coatings of 1 cm and 2 cm on these thermal bridges reduces the windows offset energy load by about 24–50%. A relevant result if one considers that such thermal bridges account for an energy load percentage of the total house load around 2–8%, if not insulated.

Walker's recent study [25] concerns the thermal performance of a selection of insulation materials, suitable for historic buildings. The paper concludes that aerogel outperforms most of the other insulators in terms of  $\lambda$  (0.016 W/(m·K)), and thermal diffusivity, showing the greatest U-value improvement of 61%.

Alternative research efforts suggest how to overcome cost and process impacts of aerogel supercritical drying by adopting an innovative route for preparation of hydrophobic silica aerogels via ambient-pressure drying adopting sodium silicate as a precursor and relatively low process temperatures [26].

## 2.2. Phase-change materials for building purposes

Several research studies have been investigating, in recent years, the integration of latent thermal energy storage systems in building envelopes, with the purpose of achieving improved energy savings in buildings. PCMs are chemical compounds which remain in either solid or liquid state at atmospheric conditions, tending to solidify or melt depending upon the thermal load being extracted or supplied [27]. The heat of fusion of the PCM represents the change in internal energy taking place during the phase transformations. The main objective of PCM use is to customize an optimized redistribution of the thermal loads in buildings. As observed by Su et al., [28], lower melting temperatures can be obtained in organic, salt hydrate, eutectic and solid-solid PCMs, whereas inorganic and metallic PCMs show higher melting temperatures. Moreover, the latter also have low heat storage capacity. The main factors influencing the effectiveness of PCMs' applications are suitable phase transition temperature, high latent heat of transition per unit weight, high  $\lambda$ , large specific heat capacity. A class of widely used organic solid-liquid PCMs is represented by paraffin materials, belonging to a family of saturated hydrocarbons, containing straight hydrocarbon chains ( $C_nH_{2n+2}$ ), whose length proportionally affects the melting temperature. Among non-paraffin organic PCMs are fatty acids, i.e. compounds of carbon (C), hydrogen (H) and oxygen (O). Among inorganic PCMs, salt hydrates are the most thoroughly studied class. They are alloys of inorganic salts and water forming a typical crystalline solid. The standard characterization techniques for PCMs performance – both in large scale and in small scale – are represented by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). As reported by Baetens et al. [5] in their review, the principle at the basis of PCMs, i.e. latent heat storage, can be applied to any porous building material. Pavlik et al. [29] highlighted the importance of microencapsulation of PCM in order to avoid the leakage of the material in its liquid phase, but also to increase the heat transfer area compared to macrocapsules. They investigated lime plaster modified with Micronal PCM and pozzolana based on calcined kaoline mixed with milled mudstone. They demonstrated that the application of PCM capsules with paraffinic wax led to a significant increase of the apparent specific heat capacity in the enhanced plaster compared to the reference material. The heat flow in PCM-enhanced plaster reached about 0.6 W/g at 26.27°C (it was roughly 0.22 W/g in the reference plaster). Also Ascione et al. [30] investigated the use of PCM-enhanced plaster in the refurbishment of building envelopes, in the Mediterranean climate. A reference building was simulated before and after the refurbishment by means of PCM-enhanced plaster. The investigated parameters were phase change temperature, thickness of the PCM wallboard and location of the PCM layer within the element. The best results were obtained using 3.0 cm thick plaster on all exposures and in each of the investigated climatic conditions. The thermal behaviour of a special composite plaster was studied by Fort et al. [31], who modified the commercial dry plaster by PCM admixture (tuning the PCM weight dosages at 8, 16, and 24% respect to original dry plaster mixture). The heat storage capacity of the commercially produced lime-cement mortar was increased from 0.4 J/(g·K) to about 2.1 J/(g·K) after addition of 24% PCM.

A thorough investigation of the properties of a lime plaster incorporating PCM was proposed by Pavlick et al. [32] in 2014, reporting a high increase of the specific heat capacity at a temperature close to the PCM phase transition, for the PCM-modified plaster. Within the cooling process, the PCM-modified plaster exhibited a specific heat capacity of 1.6 kJ/(kg·K) against 0.77 kJ/(kg·K) in the reference plaster. Fiorito [33] investigated PCMs' integration in lightweight building components by means of EnergyPlus simulations. A naturally ventilated test room was modelled. The highest benefits were obtained adding PCMs in inner surfaces of walls or partitions. The benefits increased linearly with PCM thickness (though only up to 6cm).

Three novel types of organic PCMs were prepared as thermal energy storage materials for building applications by absorption of capric (CA)–palmitic acid (PA) eutectic mixture, heptadecane (HEPD) and dodecanol (DD) as different kinds of organic PCMs into pumice gypsum composite plasters were investigated by Karaipekli et al. [34]. They observed phase change in the temperature range of 21.0–23.3 °C and structural stability even after 3000 cycles.

Lee and Medina [35] recently simulated a frame wall in which PCM (hydrated salt with melting and solidification temperatures in the range of 27.6 °C–29.6 °C) was macroencapsulated in containers larger than 1 mm, as a suitable strategy to reduce the elevated on-peak demand from air conditioning in the state of California. The developed numeric model predicting heat transfer across residential walls enriched with PCMs was validated against experimental data in test-houses. In total energy consumptions, the savings from using the PCM-enhanced frame walls resulted in 5.61 kWh/(m<sup>2</sup>·yr) as the average for the coastal climates and 9.21 kWh/(m<sup>2</sup>·yr) for the transitional climates. Navarro et al. [36] used the internal slab as storage unit and as an active cooling supply to replace totally or partially conventional HVAC systems in Spain. PCM was macro-encapsulated in 1456 aluminium tubes of 12 mm diameter containing 52

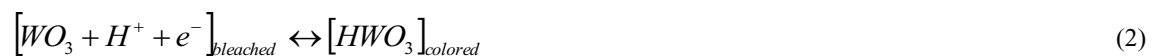
kg of RT-21 paraffin. Energy savings in the HVAC system were registered, between 30% and 55% under mild conditions, and between 15% and 20% under severe conditions, compared to a reference cubicle. Further research activities should, among the other objectives, achieve the narrowest possible temperature range for the phase change process in PCMs and reduce their costs [37].

With these premises, the application of nanotechnology aiming at an enhancement of PCMs' performances is a natural evolution. As abrupt changes in thermophysical and physicochemical properties occur at nanoscale level, current research activities are aiming at the exploitation of nano-enhanced features of PCM materials. Such emerging field was thoroughly reviewed by Parameshwaran [27]. Inclusion of nanomaterials, for instance, could improve some PCM characteristics, overcoming some intrinsic limitations, such as low  $\lambda$  [38]. Nano-enhanced PCMs embodying copper, but also titania, alumina, silica and zinc oxide nanoparticles (NPs) were investigated by Teng et al. [39]. They observed that TiO<sub>2</sub> NPs were more effective than the other additives in enhancing heat conduction and thermal storage in paraffin, also reducing the melting onset temperature and increasing the solidification onset temperature. Nano enhancement of PCMs can also follow a different approach, consisting in the encapsulation of a PCM in a nano-shell [40] or a nanofiber [41], with different preparation techniques, like electrospinning or miniemulsion. Kosny et al. [42] investigated the cost-effectiveness of PCMs inclusion in building envelopes. They found that the cost of a PCM (latent heat capacity of 116 J/kg), while produced commercially, has been projected to be around 4.4-6.6 USD/kg. Furthermore, a non negligible aspect is represented by the effort to design environmental-friendly PCMs for building applications. Kang et al. [43] prepared Bio-based PCMs made from underused feedstock, such as soybean oil, that are significantly less flammable than paraffins. Research perspectives for nano-PCMs include the preparation of nanostructures prepared in customized ranges of size (to get the desired thermal energy storage capabilities), the standardization of PCMs' thermophysical properties, and the enhancement of bio-based PCM properties. Finally, an interesting combined design strategy was demonstrated by Berthou et al. [44] for a translucent passive solar wall exploiting either aerogel and PCMs within a unique building component having a thermal transmittance value of 0.59 W/m·K and 0.72 W/m·K, respectively for was in liquid and solid state PCM.

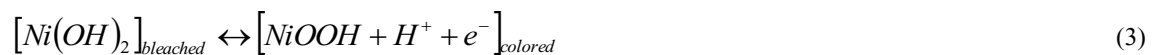
### 2.3. Chromogenic devices for building integration

Among the available chromogenic technologies, electrochromism is considered a “green” nanotechnology [45]. It has been demonstrated that such “smart windows” could produce an energy saving of 340 kWh/(m<sup>2</sup>·yr), due to the controllability of energy throughput. The EC behavior has been observed in a plethora of materials from the largely explored transition metal oxides, to conjugated polymers, and small molecules. EC oxides are typically subdivided into two main kinds: cathodic and anodic [46]. The former color under ion insertion, whereas the latter undergo an optical transition upon ion extraction, in a complementary fashion.

The most known cathodic EC material is tungsten oxide (WO<sub>3</sub>). A typical anodic inorganic EC oxide is nickel oxide (NiO). The basic redox reactions of cathodic (and anodic) electrochromism can be simplified with the elementary reactions (2) and (3), regarding WO<sub>3</sub> and NiO [46]:



And



EC devices [47,48] containing transition metal oxides consist typically of a multilayered battery-like architecture [49]. This research field has catalyzed the attention of several research groups worldwide, dating back to the 80's. An EC device generally contains substrates, transparent conductive oxides, an ion conductor and one or two EC materials. Optical absorption varies when electrons are inserted (extracted, in case of anodic EC materials) into the cathodic EC material from the transparent conductive oxide and charge balancing ions enter from the electrolyte (or exit, respectively, in the case of anodic ECs).

PEC devices represent indeed an intriguing class of “smart” devices [50]. They are capable of sensing even small changes in external irradiation, undergoing, consequently, a perceivable change in transmittance. PEC devices inspire optimistic expectations to design “intelligent” building envelopes, able to manage the complex energy flows intercepted by them. Dynamic tintable PEC windows could determine a consistent energy consumption attenuation, a reduction of cooling loads, also lowering the demand for electric lighting [51].

In their seminal letter to Nature, Bechinger et al. [52] described the first PEC device, embodying a ruthenium sensitized nanocrystalline titanium dioxide photoelectrode and a tungsten oxide layer, deposited by thermal evaporation on the counter electrode. The former, acting as a light-absorber, produced an open circuit voltage of 0.6–0.9 V, which was a sufficient driving force to move electrons into the WO<sub>3</sub> film; the charged counter electrode, in short-circuit conditions, attracted lithium ions in the octahedral structure of WO<sub>3</sub>, activating its reversible coloration. PEC devices could work requiring no external energy supply, apart from the electric power generated by the device itself.

Hauch et al. [53], from Fraunhofer-ISE, proposed a new PEC cell, showing some architectural novelties: the photoactive (TiO<sub>2</sub>) layer was deposited directly onto the electrochromic layer (WO<sub>3</sub>), thus sharing the same electrode. They reported the activation of a consistent coloration mechanism at open-circuit conditions (under 1 sun illumination), taking place within 2 min (for colouring and bleaching). Later, in 2009, Wu et al. [54] disclosed the first ever PVC devices, i.e. solar cells combining the photovoltaic properties of dye-sensitized cells and PEC properties of the initial Bechinger’s PEC cells. Such devices colored in short-circuit conditions under light irradiation, showing very fast coloration (4 s), and fair photovoltaic characteristics ( $\eta=0.50\%$ ). A fast bleaching time was also demonstrated (about 40 s), due to the presence of the platinum catalyst. It was the first demonstration of a glass showing smart coloration and photovoltaic characteristics as well.

An innovative design for PVCs was proposed by Cannavale et al. in 2010 [55], with a specifically designed counter electrode, (a C-shaped platinum frame bounding a square WO<sub>3</sub> region): the two areas were electrically separated, in order to allow distinct operations on the two available external circuitries. We obtained smart control of optical transmittance modulation and, at the same time, a dramatic increase of photovoltaic efficiency respect to previous PEC devices reported in literature ( $\eta=6.55\%$ ). A further approach was developed in 2014, with a comb-like pattern for bi-functional counter electrodes, consisting of two physically separated series of stripes made of tungsten oxide and platinum, respectively, resulting from the combination of physical vapor deposition and lithography-based microfabrication processes [56]. The generated photovoltage could drive electrons into the electrochromic stripes, under illumination. Lithium intercalation was promoted, with very fast coloration (2 s) and bleaching (5 s) times. The photovoltaic circuit enabled a fair solar energy conversion efficiency, especially affected by the dye adopted and the WO<sub>3</sub>/Pt area ratio. Highly transparent organic dyes, suitably designed, were adopted, in view of potential building integration purposes. More recently, we proposed a semi-transparent perovskite photovoltaic film with a solid polymer electrolyte-based electrochromic device to achieve a solid PVC device. The top glass had both sides coated with TCOs, working as separated electrodes. On the other hand, the bottom glass has only one conductive layer, with e-beam deposited WO<sub>3</sub> on top. A solid polymer electrolyte, based on polyethylene oxide plasticized by means of PEG, acted either as an effective electrolyte for the electrochromic part of the device and as a suitable “glue”, laminating the two substrates [6]. The photovoltaic layer showed high transmittance, due to the customized dewetting of the perovskite islands, allowing the formation of discrete micron-sized islands. PV conversion efficiency of 5.5% and optical modulation of 26% were observed in these devices. A self-activated tinting was enabled, according to the available irradiation, with the additional possibility to deliver external power.

Dynamic tinting gradient can also increase indoor visual comfort, allowing visual interaction with the outside even when operating as a shading system. Effectiveness of the integration of PVC devices in windows was also studied [7] predicting an increase of UDI of up to about 72% as an average value in a standard office room. An additional demonstrated benefit was the reduction of intolerable glare to less than 12% of occupied hours.

### 3. Conclusion

The reviewing activity provides an investigation of the most recent results, opportunities and open issues concerning three available technologies for opaque and transparent building envelopes: aerogel, PCMs, EC and PEC devices. Figures of merit, material characteristics, processing and cost considerations are exposed for each of these pivotal

technologies, identifying further research opportunities to optimize the exploitation of nanomaterials and nanodevices in the construction process. So far, BIPV has encountered several barriers to their industrial exploitation. They were not only, unexpectedly, due to technological and economic aspects. Severe obstacles to the diffusion of innovative PEC technologies, as in the case of BIPV, have also arisen from merely aesthetic and psychological assumptions, thus limiting the use of available technologies, even if effective and non-expensive. PEC or PVC devices could give a strong stimulus to building integration of innovative components, profiting of their manifold outcomes of multifunctional devices, with their consequent economic, technologic, aesthetic and maintenance advantages. We firmly believe that an optimal design strategy of multifunctional building components could profit of the most recent outcomes of research activities in the field of materials science, with relevant effects on comfort and energy consumption in buildings.

## Acknowledgements

AC acknowledges Regione Puglia and ARTI for funding this research project within “FIR - Future In Research projects”.

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