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Original

Passive daytime radiative cooling / Pattelli, Lorenzo; Papakonstantinou, Ioannis. - In: PHOTONIQUES. - ISSN 1629-4475. - 128(2024), pp. 56-61. [10.1051/photon/202412856]

Availability:

This version is available at: 11696/82339 since: 2024-11-28T09:44:28Z

Publisher:

EDP Sciences

Published

DOI:10.1051/photon/202412856

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PASSIVE DAYTIME RADIATIVE COOLING

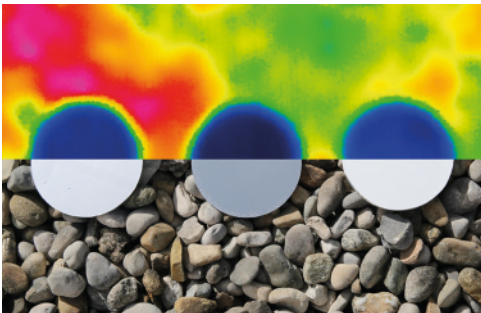
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<https://doi.org/10.1051/photon/202412856>

With average global temperatures constantly increasing, the emerging field of passive daytime radiative cooling holds promise to alleviate our growing cooling needs and protect the environment by providing us with electricity-free cooling power. Here, we briefly revise the principles behind this rapidly expanding field, its main material platforms and implementations, and its outstanding challenges in terms of scalability and durability against weathering agents.

Pointing a thermal infrared camera towards the sky reveals an interesting fact: even during a hot summer day, sub-freezing temperatures can be observed with clear sky conditions. Thermal cameras are sensitive to infrared wavelengths at the peak of the blackbody emission of objects at near-ambient temperature. At these very same wavelengths, our atmosphere happens to be almost transparent, so that pointing the camera at the sky reveals the coldness of outer space. From an opposite perspective, this is what allows thermal satellite imagery of our planet to be acquired from space: a significant part of infrared radiation emitted from the Earth's surface can escape freely through the atmosphere, with a clear sky effectively acting as a radiative heat sink able to dissipate arbitrary amounts of thermal

radiation. Morning frost formation on grass or a car windshield despite above-freezing temperatures are common manifestations of this passive radiative cooling effect. In fact, nighttime radiative cooling has been exploited for thousands of years, allowing ancient populations to produce ice also under adverse climates where temperatures would not typically allow it.

The same refrigeration mechanism, in principle, is equally active also during the day, even though in this case its effect is more than offset by the strong irradiance coming from the Sun. Just 10 years ago, however, pushed by the relentless progress in the fabrication of micro- and nano-structured materials, a new milestone was finally demonstrated. By shielding a material from environmental convection and conduction heat gains, and engineering it in such a way to reflect all solar light and emit

radiation selectively at the wavelengths in the atmospheric transparency range, spontaneous sub-ambient cooling was demonstrated for the first time under a peak solar irradiance of almost 900 W m⁻² [1].

Due to its relevance as a renewable and largely untapped source of electricity-free cooling power, interest around passive daytime radiative cooling (PDRC) surged, with several research groups and private companies worldwide working on this topic [2].

FUNDAMENTALS OF PDRC

To achieve passive daytime radiative cooling, the emitter must exhibit a low emittance (i.e., high reflectance) across the whole solar and infrared spectrum, except at wavelengths where the atmosphere is transparent (Figure 1). In order to deliver a net daytime cooling power, however, the full energy balance

must be positive:

$$P_{\text{rad}} - P_{\text{atm}} - P_{\text{solar}} - P_{\text{nonrad}} > 0$$

where P_{rad} is the power irradiated by the sample, P_{solar} and P_{atm} are the absorbed powers from the sun and the atmosphere, while P_{nonrad} is the total power gain from all non radiative heat transfer processes, such as conduction and convection to the external environment.

For daytime applications, the power absorbed from the sun $P_{\text{solar}} = \int_{0.3\mu\text{m}}^{4\mu\text{m}} I_{\text{solar}}(\lambda)\epsilon(\theta, \lambda)d\lambda$ must be minimized, with $\epsilon(\theta, \lambda)$ being the spectral emittance of the sample for incident solar illumination at an angle θ . Considering that global solar radiation can exceed 1000 W m^{-2} , and that an ideal selective emitter can achieve at best about $100\text{-}150 \text{ W m}^{-2}$ of net cooling power under dry and clear sky conditions, the average solar reflectance must be larger than 0.9 and more likely larger than 0.95

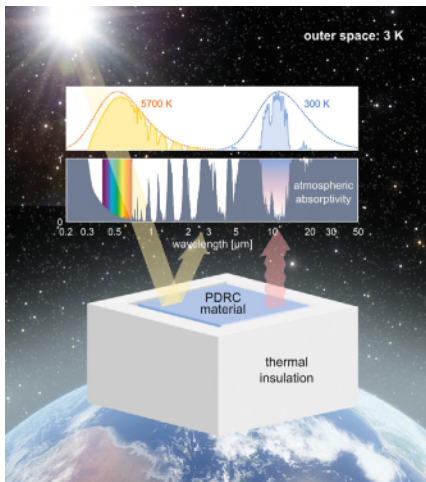
for any material to exhibit a measurable net cooling power under typical atmospheric conditions.

Non-radiative heat transfer contributions are often combined into a single term $P_{\text{nonrad}} = h(T_{\text{amb}} - T_s)$ where h is the total heat transfer coefficient accounting for both convection and conduction between the sample and the environment, with typical values of a few $\text{W m}^{-2} \text{ K}^{-1}$ for well insulated, low wind conditions. Conversely, the radiative balance is determined by the balance between P_{atm} and P_{rad} .

The power absorbed from the downwelling atmospheric irradiance depends on the coating emittance, atmospheric emittance and the atmospheric (ambient) temperature as

$$P_{\text{atm}}(T_{\text{amb}}) = \int_0^{\pi/2} \cos\theta d\Omega \int_0^\infty I_{\text{bb}}(\lambda, T_{\text{amb}}) \epsilon_{\text{atm}}(\Omega, \lambda) d\lambda$$

where $\epsilon_{\text{atm}}(\Omega, \lambda)$ is the atmospheric emittance as a function of direction and wavelength and $\int d\Omega = \int_0^{\pi/2} \int_0^{2\pi} \sin\theta d\theta d\phi$



The radiative heat balance of a passive radiative cooling emitter results from the interplay between several factors. A first important requirement is to shield the emitter from ambient conditions, insulating it from any non-radiative (*i.e.*, conduction and convection) heat gains coming from the environment, leaving only an open aperture towards the sky. Secondly, to ensure cooling during daytime hours, the emitter must exhibit near-

perfect reflectance across all solar wavelengths, and near-perfect absorptivity (and hence, emissivity) between 8 and $13 \mu\text{m}$, where molecular gas species in the atmosphere lack significant absorption bands and thermal radiation is free to escape to outer space. Following Kirchhoff's law of thermal radiation, any object at thermodynamic equilibrium with its environment must be characterized by an equal absorptivity and emissivity following a detailed balance principle imposed by reciprocity considerations. At wavelengths in the infrared transparency window, the downwelling irradiance from atmospheric gas species is very low, as well as that from outer space. Hence, the equilibrium condition for a selective perfect absorber/emitter exposed to the clear sky will shift towards sub-ambient temperatures, leading to a net passive radiative cooling effect.



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is the angular integral on the upper hemisphere. A small atmospheric emittance (or large transmittance) is found between 8–13 μm, dubbed as the LWIR transparency window (see Insert). The effective transparency in this range depends on several factors including the zenith angle, cloud cover, humidity, aerosol and pollution, with more downwelling irradiance received during cloudy or humid weather.

Similarly, the radiative power of a PDRC coating is a function of its temperature and emittance spectrum

$$P_{\text{rad}}(T_s) = \int_0^{\pi/2} \cos\theta \, d\Omega \int_0^\infty I_{\text{bb}}(\lambda, T_s) \varepsilon(\Omega, \lambda) \, d\lambda$$

where $I_{\text{bb}}(\lambda, T_s)$ is the spectral intensity emitted by a standard blackbody at temperature T_s . The peak of blackbody emission is located inside the atmospheric LWIR window for typical ambient temperatures, allowing the dissipation of a large fraction of P_{rad} directly to outer space. Considering that T_s and T_{amb} are similar, the balance between P_{atm} and P_{rad} is dominated by the radiative power exchange between 8 and 13 μm, where the atmospheric irradiance is lowest (see Fig. 1). When $T_s < T_{\text{amb}}$, a selective emissivity from the sample is key to avoid absorbing the strong P_{atm} outside of the LWIR

window. Conversely, when $T_s > T_{\text{amb}}$, broadband emissivity over the whole thermal range leads to an increase of P_{rad} which can be particularly useful in above-ambient cooling scenarios (e.g., cooling of photovoltaic modules, heat-pump condenser units, data centers, etc.). For characterization purposes, the net cooling power is typically calculated by taking $T_s = T_{\text{amb}}$, since under this condition P_{nonrad} vanishes.

SELECTION AND DESIGN OF PDRC MATERIALS

Based on the above power balance relation, any PDRC material must comprise several elements guaranteeing a strong reflectance at solar wavelengths, a high emittance in the LWIR atmospheric window, and ideally some degree of thermal insulation from the environment.

Regarding solar reflectance, two main mechanisms exist involving either a metal-based reflector (typically silver, due to its high solar reflectance), or a diffuse reflector exploiting random and/or hierarchical structures to ensure high reflectance over the broad solar wavelength range (see Figure 2). In the former case, a separate emitter must be added on top of the silver mirror due to the low emissivity of metallic reflectors,

as well as a convection shielding membrane. This is a prototypical configuration where each function of a PDRC material is embodied by a dedicated layer. Several examples in the literature belong to this family, with emitters of different types ranging from 1D dielectric stacks, to flat polymer films, photonic metasurfaces or host layers with highly emissive inclusions, to name a few. Conversely, different architectures can emerge when multi-functional layers take on multiple roles. For instance, one can avoid using metal reflectors by delegating solar reflectance to a highly scattering and yet IR-transparent top layer, such as those obtained with porous polyethylene membranes. Alternatively, a single layer can be both highly reflective at solar wavelengths, and highly emissive in the LWIR window. Many examples are known for this class of PDRC materials, ranging from porous polymer mats and aerogels, to paint-like formulations, electrospun membranes, sintered ceramics or delignified wood layers, even though these materials may present very different degrees of thermal resistivity against the substrate where they are applied, and from which they are supposed to drain heat.

Depending on the architecture, an array of materials with specific properties has been explored in the recent literature [4, 5]. For instance, IR-transparent materials used as convection shields are typically made of polyolefins such as polyethylene thanks to their structure containing only saturated aliphatic bonds which do not absorb between 8 and 13 μm. Materials such as ZnS or ZnSe have also been used as infrared windows for de-pressurized chambers used to test PDRC materials in the absence of convection.

Regarding emitting layers, polymers with functional groups such as -CH₃, C-O, C-OH, C-O-C all have useful resonances within the atmospheric transparency range, as well as the -CF₃ group

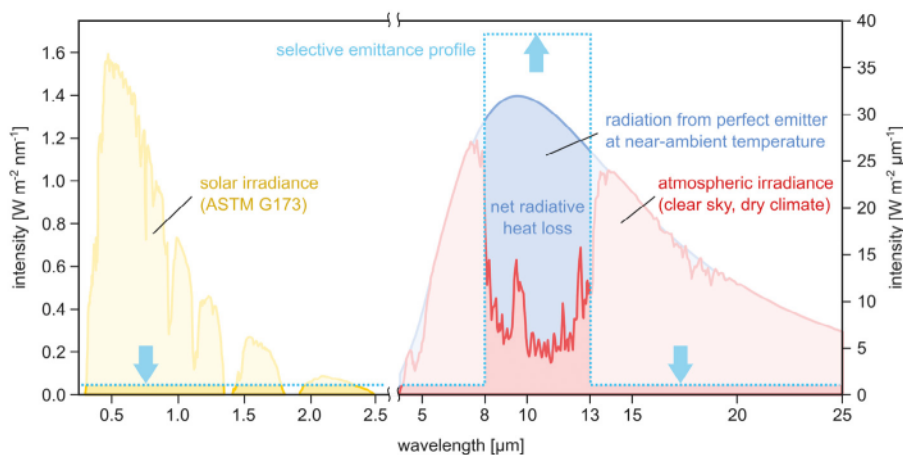


Figure 1. Spectral properties for an ideal passive radiative cooling material, compared to the solar spectral irradiance (yellow) and atmospheric downwelling irradiance (red). By reflecting all radiation outside of the atmospheric LWIR window (8–13 μm), a net radiative heat loss towards the sky sink is obtained considering the blackbody emittance spectrum of a typical object at near-ambient temperature.

present in perfluorinated polymers. The Si–O–Si bond present in silica and polysiloxanes, or the Si–N–Si in polysilazanes are also strongly absorbing in the LWIR window, while bonds such as C=O, C=C, C=N or –CHO should be avoided, as they have resonances outside the atmospheric transparency window and can thus absorb the downwelling atmospheric irradiance.

Several polymers with a desirable mix of such resonances have been identified, such as poly(vinylidene fluoride-co-hexafluoropropene) (P(VdF-HFP)), poly(tetrafluoroethylene) (PTFE) or polyvinyl fluoride (PVF), to name a few. Fluorinated polymers offer high durability against weathering and chemical agents, UV degradation and soiling. However, their extreme persistence raises increasing concerns for health and environmental protection, with a pending EU-wide proposal to ban the use of all per- and poly-fluorinated alkyl substances. Prominent alternatives exist such as polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), polyvinylchloride (PVC), polysilazanes, or poly(4-methylpentene) (TPX) – all the way to biological polymers such as cellulose or chitin, even though their possible degradation with UV light typically requires the use of additives to increase their durability.

In addition to organic polymers, inorganic materials also serve a key role in the development of new PDRC coatings. Endowed with both a higher refractive index than typical polymers and strong absorption resonances at LWIR wavelengths, many of these materials are also chemically inert, non-toxic, and with high mechanical and UV resistance. To minimize solar absorbance in the UV, inorganic compounds with a band gap energy above 4.13 eV (corresponding to a wavelength of 300 nm) are most relevant, such as ZrO_2 , Y_2O_3 , h-BN, $CaCO_3$, $BaSO_4$, Al_2O_3 or SiO_2 . Depending on the envisioned application, some of these materials may be limited by their high density (such as yttrium oxide) and their scarcity as a critical raw material (such as barium), while others can find use in

a range of extreme applications despite their moderate or low refractive index (Al_2O_3 or SiO_2), allowing to form fire-resistant porous ceramic materials [6].

APPLICATIONS AND CHALLENGES TOWARDS COMMERCIALIZATION

Developing new fabrication methods and strategies to combine these materials and exploit their complementary optical and thermophysical properties is instrumental to exploring new PDRC applications, as they extend across different areas and may require a diverse range of features. For instance, PDRC coatings can significantly enhance the conversion efficiency and lifetime of photovoltaic modules by lowering their operation temperature. In this case, however, they should not block all solar radiation but only those wavelengths that are not efficiently converted to electricity. Additionally, due to the above-ambient PV cell temperatures during the peak of the day, broadband rather than selective emissivity should be preferred, and convective losses should be favored as an additional cooling mechanism. Thus, depending on the application, different material properties become desirable.

In addition to the straightforward use of PDRC materials for energy savings in the building sector, other prominent applications include cooling clothing and textiles for personal thermal management, as well as cold storage applications combining both daytime and nighttime cooling for the peak-shifting of cooling-related energy needs. Continuous 24h thermoelectric generation enabled by the temperature gradient offered by PDRC materials has been demonstrated, as well as 24h water harvesting by condensation of air moisture. Water desalination by either evaporation or cascaded freezing stages has been shown, and new applications are being considered for ice and food preservation, as well as for more efficient water use in greenhouses, or for the cooling of electronic devices, batteries or power distribution boards.

Meeting the diverse requirements for all these applications remains still challenging to date. Due to the ●●●



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inherent working principle of the sky cooling mechanism, these materials must be able to withstand prolonged outdoor exposure, where even slight contamination of their surface properties can quickly nullify their cooling function. For this reason, considerable efforts are being devoted to developing coatings that are super-hydrophobic and/or amphiphobic, with low roll-off angles allowing their self-clean under rain or water rinsing. Inorganic coatings or additives such as dyes, emitters or radical scavengers are added to mitigate UV aging, with multi-layered structures being developed to trade off part of the spectral performance for a longer durability and resistance to scratches, abrasion or better adherence to the substrate.

Finally, one of the main outstanding challenges towards the widespread adoption of PDRC materials is related to their industrial scalability [7]. Still to date, most of the results in the literature are based on specimens with a lateral size of a few cm, even though rapid progress is being made by adapting already existing fabrication technologies to the materials relevant for PDRC applications. Phase separation and blade coating processes can be scaled up to continuous roll-to-roll fabrication of multi-layered film structures. Multiple inorganic thin layers can similarly be deposited by a continuous PVD process to form selective emitters. Certain PDRC paint formulations can be sprayed directly onto a substrate, even though work is still needed to minimize the use of volatile organic solvents required to reach the high particle volume concentrations typical of these paints. Finally, fiber-spinning techniques have also been proven as a cost-effective and scalable strategy for the production of large-area PDRC materials.

A growing number of startups and larger companies are currently approaching the market with new PDRC materials, which will foster

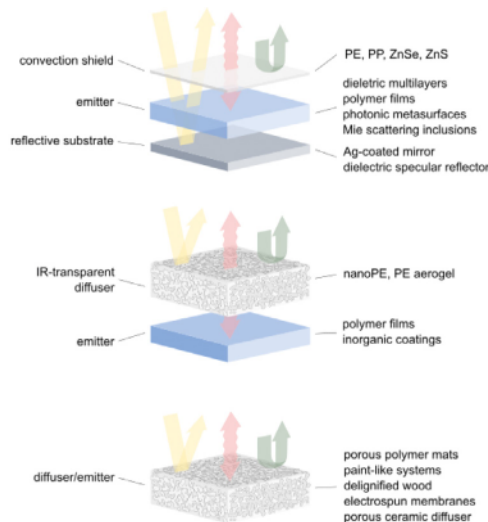


Figure 2. General classification of PDRC material architectures. From top to bottom, different options can exist, based on whether solar reflectance is provided by a metallic mirror, a porous IR-transparent membrane, or a strongly emitting disordered layer.

the development of more stable and scalable solutions, but also raise the question of how to evaluate in a comparable way the cooling performance of this new class of products.

CONCLUSION

In a world with quickly increasing cooling needs, passive daytime radiative cooling stands out as a unique sustainability opportunity enabled by photonics. Compared to all other cooling technologies, it is the only one capable of providing

a net refrigeration by directly expelling heat from the planet, rather than discharging it into the environment. Nonetheless, many scientific challenges still require further research efforts, such as finding new ways to mitigate convective heat gains, pollution or dust contamination. Additional limitations of PDRC materials are related to their aesthetics and visual comfort due to their glaring appearance, as well as their static cooling functionality, even though new structurally colored or self-adaptive materials are quickly emerging, which can modulate their spectral properties based on external stimuli. Multi-disciplinary approaches are needed for the advanced fabrication and characterization of this new class of materials, driven by the fast progress of photonic structures with selective spectral properties optimized over the broad wavelength ranges encompassing both solar and thermal radiation. ●

ACKNOWLEDGMENTS

L.P. acknowledges support by the European project 21GRD03 PaRaMetriC, which received funding from the European Partnership on Metrology, co-financed by the European Union's Horizon Europe Research and Innovation Programme and from the Participating States. I.P. acknowledges financial support from the ERC-PoC PolyCool.

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