New materials for the recovery and storage of thermal energy

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Summary. — A significant fraction of the energy generated for industrial and domestic applications is lost in the form of heat. Because of this, thermal-energy storage materials are receiving increasing attention as a means of storing the generated heat for later use. In this paper, a brief description is given of two types of materials used in thermal-energy-storage devices —phase change materials for latent heat storage and photoswitches for chemical energy storage. In addition, we provide a succint account of the experimental and computational tools needed to understand the microscopic mechanisms of energy storage and to facilitate the rational design of new materials.

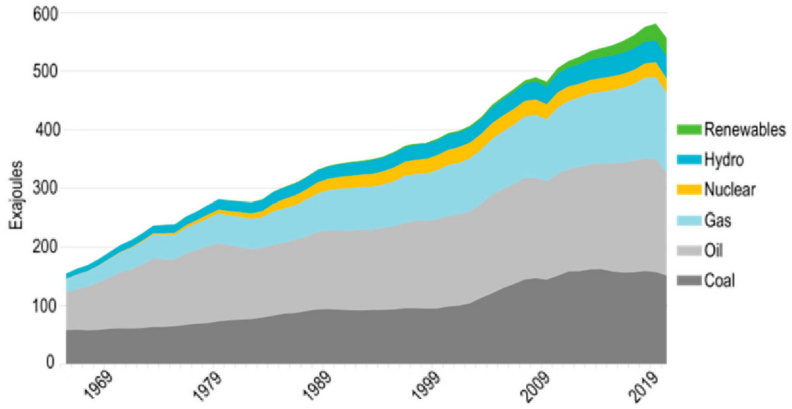

Fig. 1. – Global energy consumption over the period 1965–2020. Adapted from ref. [2].

1. – Introduction

World energy demands have increased and continue to increase quite considerably over the past 60 years, reaching a global energy consumption of ~ 600 Exojoules (6×10^{20} J) in 2019 [1]. As illustrated in fig. 1, there are no visible signs that such a trend will change in the foreseeable future. Fossil fuels still dominate electricity production ($\sim 80\%$ of the global energy consumption, see fig. 1) [3], but they are not sustainable in the long term and have a dramatic negative impact on the environment. In addition, a significant fraction of the energy that we produce for industrial and domestic use is lost in the form of heat, in some situations amounting to as much as one-half of the total energy input [4,5]. As a consequence, and within the EU commitment to achieve climate neutrality by 2050 [6], there is an ongoing effort to transform the current energy ecosystem into one based on renewable sources, and to implement policies and technologies leading to a more rational and efficient use of energy.

In this respect, thermal-energy storage (TES) technologies [7] can help to accomplish the goal of climate neutrality in two ways. First, they can be used to prevent heat loss in conventional energy production schemes giving it a subsequent efficient use. Secondly, they can contribute to make a real and effective deployment of renewable energy production technologies by bridging the existing gap between generation surplus and peak demand, which is currently impossible to achieve without energy-production infrastructures based on non-renewable sources. In this contribution, a brief introduction is given on the different strategies to TES, with an emphasis on emerging classes of materials and the experimental and computational tools used to explore them.

2. – Thermal-energy storage materials

TES technologies can generally be classified into three types: latent-heat storage (LHS), thermo-chemical storage (TCS) and sensible-heat storage (SHS). In this brief account, we place a focus on TCS and LHS, as they are receiving an increasing amount

TABLE I. – *Examples of organic (left) and inorganic (right) PCMs, their melting point (T_m, in K), latent heat of fusion (ΔH_m, in $J\,g^{-1}$) and thermal conductivity in the liquid state (κ_L, in $W\,m^{-1}\,K^{-1}$)* [7, 12-14].

Material	T_m	ΔH_m	κ_L	Material	T_m	ΔH_m	κ_L
Phenol	313.9	120	0.15	Na_2CO_3	1127.1	275	0.6
Acetic acid	289.7	273	0.158	K_2CO_3	1170.1	235	0.48
Paraffin wax	377.1	173.6	0.167	$MgCl_2$	1073.1	492	0.57
Polyglycol E600	295.1	127.2	0.189	KF	1130.1	452	0.65

of attention in terms of materials design relative to (more traditional) SHS strategies. For a comprehensive review of SHS, see ref. [8].

2˙1. *Phase change materials for LHS.* – LHS devices are commonly used in the building industry and in the field of solar photovoltaics for cooling. LHS relies on the heat absorbed or released when a storage material undergoes a phase change. As such, materials used in LHS devices are often named Phase Change Materials (PCMs) [7]. The most common PCMs used in applications are solid-liquid PCMs and solid-solid PCMs. Solid-gas and liquid-gas PCMs are less commonly used due to the large volume changes associated with this type of phase transition, which tends to complicate LHS design [9]. Based on composition, solid-liquid and solid-solid PCMs have been traditionally classified into organic PCMs, inorganic PCMs and eutectic PCMs [10]. Organic PCMs are particularly attractive for industrial applications, owing to their wide range of melting temperatures and compatibility with conventional construction materials. However, they tend to decompose, making implementation difficult and expensive. On the other hand, inorganic PCMs are mostly used in high-temperature applications due to their much higher melting temperatures. Nevertheless, these systems are more difficult to handle and corrosiveness can become an insurmountable hurdle. Finally, eutectic PCMs are mixtures of two or more materials at a molar ratio that minimises the melting temperature of the compound system. Their heat storage capacities are generally lower than those of organic or inorganic PCMs [7, 11]. Table I lists a few representative examples of organic and inorganic compounds used as PCMs along with physico-chemical parameters that underpin their TES performance. Other parameters not listed in this table include the reversibility as well as the kinetics of the process, *i.e.*, the speed of the phase change, yet these are far harder to quantify and translate into specific figures of merit.

There are multiple aspects to consider when selecting candidate PCMs for applications [7, 11]. These include a high heat-storage capacity per unit mass or volume as well as a high thermal conductivity, a melting temperature appropriate for the application at hand, the thermal hysteresis associated with the phase change, low cost and large-scale availability for mass production. Depending on the application, other requirements are needed, such as compatibility with construction materials, or no toxicity or flammability, particularly when used for domestic purposes [7].

2˙2. *Photoswitches for TCS*. – One of the fundamental challenges limiting most renewable energy sources is a lack of round-the-clock availability. In this respect, the excess of solar energy produced during daylight is lost if not stored efficiently. Photoswitchable molecules constitute a potential solution to tackle this challenge. They combine light absorption with energy harvesting and can work as solar thermal fuels (STFs) in molecular solar-thermal storage (MOST) applications. The underlying principle is similar to that of a spring toy: pulling the spring, the system is driven out of the minimum-energy equilibrium form and stores energy. Freeing the spring, it tends to recover its equilibrium form, resulting in toy movement. In a similar fashion, a photoswitchable molecule absorbs photons that trigger its conversion into a metastable state, which might then be able to release this stored energy upon an external stimulus, returning to its original equilibrium structure.

Efficient STFs must conform to a number of prerequisites reported in the literature [15-17]: a high quantum yield; an energy storage density above conventional heat-storage media (*i.e.* $> 0.3\,\mathrm{MJ\,kg^{-1}}$); long metastable state lifetime; and affordability in terms of abundance and price. Based on these characteristics, a range of materials have been proposed as STFs over the years, including: azobenzene and its derivatives [18-20]; norbornadiene and its derivatives [21]; or dihydroazulene [22]. However, the simultaneous optimization of all of these properties has proven challenging due to the existence of anti-correlations between them. Recent attempts to circumvent these difficulties have resorted to chemical functionalization [23] and solid-liquid transitions [24]. Although promising results have been obtained [25], achieving an STF material with an optimal balance of these properties remains a largely unresolved research problem requiring synergies across experimental and computational efforts.

3. – Exploring new TES materials, in the laboratory and on a computer

The rational design of TES materials continues to be a daunting task, requiring recourse to both experimental and computational techniques. For a given new target material, the first step is to obtain macroscopic observables associated with the desired TES performance, such as melting temperature or heat-storage capacity. At a more microscopic (atomic and molecular) level, it becomes necessary to investigate its structure and dynamics in the laboratory in order to relate them to performance. Once this information is known, computational modeling becomes a key player (once validated by experimental data), to interrogate the details of the mechanism of phase transformations.

To determine the heat storage capacity and melting temperature of PCM candidates, the most common technique used nowadays is Differential Scanning Calorimetry (DSC). In this technique, the temperature of both the PCM and a reference (commonly aluminium) is changed by inserting them in a furnace or heating unit, and the heat-flow rate of both is monitored. A phase change will be seen as a rapid change in the heat-flow rate over a narrow temperature range. For further details on the principles and methodologies behind DSC, the reader is referred to refs. [26-29]. Standard DSC studies involve heating and cooling speeds in the range 0.1–$300\,\mathrm{K\,min^{-1}}$. More recently, the develop-

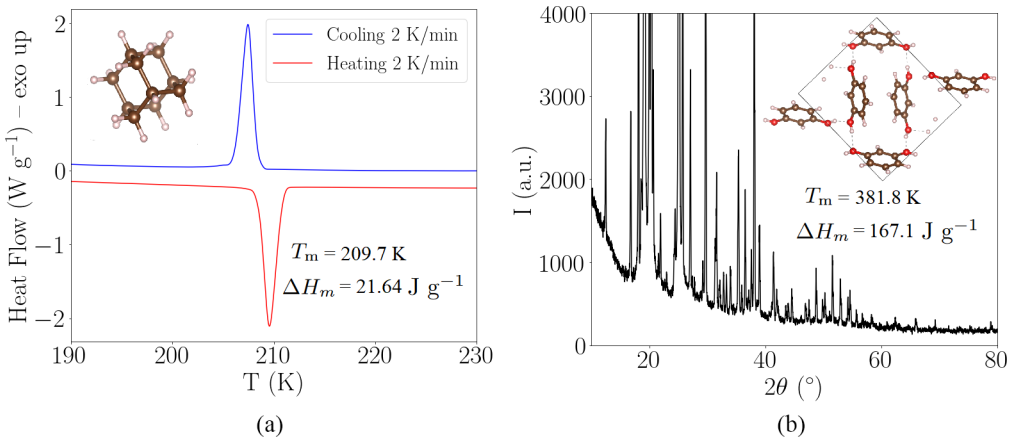

Fig. 2. – (a) DSC data of adamantene. The inset shows its molecular structure, melting point (T_m) and latent heat of fusion (ΔH_m). Note the slight, yet clearly discernable, hysteresis upon heating and cooling. These effects are related to the reversibility of the phase change. (b) X-ray diffraction pattern of a polycrystalline specimen of resorcinol. The inset shows the crystal structure of resorcinol derived from these data, the melting point (T_m) and the latent heat of fusion (ΔH_m).

ment of Fast Scanning Calorimetry (FSC) has enabled measurements at much faster rates. An example of a FSC instrument is the Flash DSC designed by Mettler-Toledo, with ultra-high heating and cooling rates —from 30 K min^{-1} to 3 000 000 K min^{-1} over the temperature range 178–1273 K. Such fast cooling and heating rates allow access to entirely new phases of the material with new and improved properties. For further information on FDSC, the reader is referred to refs. [30, 31]. Figure 2a shows an example of DSC on a molecular material at cooling and heating rates of 2 K min^{-1} and ref. [32] provides a recent illustration of the combined use of DSC and FSC on a series of molecular materials. To study the structure of these systems at a molecular and atomic level, X-ray and neutron scattering are the most commonly used techniques [33]. An example of an X-ray diffraction pattern of the PCM candidate resorcinol (meta-dihydroxybenzene) is shown in fig. 2b. In addition, inelastic-scattering techniques combined with spectroscopic techniques such as Raman and FTIR (Fourier-transform infrared) are used to study both dynamics and local structure. For further details on scattering techniques, Raman spectroscopy and FTIR spectroscopy, the reader is referred to refs. [33-37].

Computational materials modelling has become a key addition to the aforementioned experimental techniques. In the solid state, density functional theory (DFT) [38] has become the most widespread method, particularly for the study of crystalline structures with well-defined long-range order. There are conceptual reasons that make DFT appealing yet, aside from those, there is also a pragmatic aspect: state-of-the-art implementations of DFT are in general less computationally demanding than those of highly correlated wavefunction-based methods. This advantage allows the computation of structural

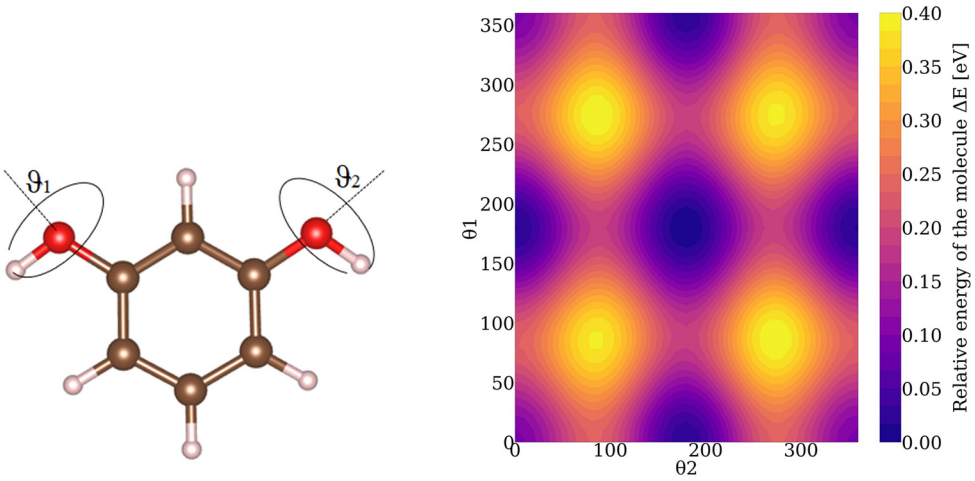

Fig. 3. – (a) Molecular structure of resorcinol – carbon (brown), oxygen (red), hydrogen (while). (b) Contour map of the relative energy of the molecule as the hydrogens rotate around the oxygens, using the angular variables defined in (a).

observables amenable to scrutiny in the laboratory for both molecular systems and crystals. In addition, DFT can also disentangle dynamical quantities with the framework of molecular dynamics (MD). Typically, this is done within the Born-Oppenheimer approximation that treats the atomic nuclei as classical particles obtaining their trajectories by solving Newton's equation of motion. Hence, the analysis of the experimental data is carried out in a robust and quantitative manner and provides a wealth of information for the characterization of diverse phenomena, including phase transitions enabling energy storage, chemical reactions and light-matter interactions. Figure 3 shows DFT calculations of how the relative energy of a single molecule of resorcinol (also featured in fig. 2b above and in ref. [32]) changes as the O-H arms (red-white spheres in the figure) are rotated around an axis. These DFT calculations allow us to find what is the structure of the molecule with the lowest energy, *i.e.*, the most stable structure in a given phase. An alternative way to simulate large systems (*i.e.*, liquid state and disordered solid phases) is provided by hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) and QM/MM/MD approaches. In the simplest formulation, a typically small part of the system is described using QM methods, to characterize processes not captured at the classical level. The rest of the system is described at the MM level employing a force field. The interaction between both parts is incorporated using different coupling schemes [39], which address quantum mechanical effects in the fragment of interest at a reasonable computational cost. Finally, when investigating processes in molecular systems that involve excited states such as photoswitching in STFs, specific methods have to be used. In this context, time-dependent DFT methods (TDDFT) [40] are a cost-effective option. However,

state-of-the art TDDFT approaches have well-known limitations and cannot be applied systematically to all molecular systems and processes of interest. For those cases where TDDFT fails, wavefunction-based methods such as multireference perturbation based techniques [41] can be used, although at a (usually) much higher computational cost.

4. – Conclusions and outlook

On the whole, there is a growing and increasingly collective drive in the global scientific community to rationalize the design of new materials for a more efficient use of energy and their integration with renewable sources. Exploring and ultimately controlling the performance of new materials require combined experimental and computational efforts, and these are beginning to shed new light and important insights not amenable to scrutiny not so long ago. Our hope is that these brief lecture notes on current efforts to discover new materials for thermal-energy storage will inspire some in the audience to join the cause.

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T.S.N.F is grateful for financial support from the Donostia International Physics Center to attend and participate in the Joint EPS-SIF International School on Energy 2023, leading to these lecture notes. Financial support for this work has been secured through Grants PID2020-114506GB-I00 funded by MCIN/AEI/10.13039/501100011033; TED2021-129457B-I00 funded by MCIN/AEI/10.13039/501100011033 and the European Union NextGenerationEU/PRTR; EC-2022-1-0019, funded by the Basque Government; and RES-QHS-2023-1-0027, supported by the Red Española de Supercomputación for access to computer resources at XULA-CIEMAT. A.O.R thanks the Principality of Asturias (FICYT) for project AYUD/2021/51036, cofinanced by EU FEDER. M.G. acknowledges the support of Chiara Milanese from the University of Pavia. We also acknowledge the continued support received from the IKUR Strategy under the collaboration agreement between Ikerbasque Foundation and the Materials Physics Center on behalf of the Department of Education of the Basque Government.

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