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An Energy Transition To Save The Planet

Vincenzo Balzani, Editor

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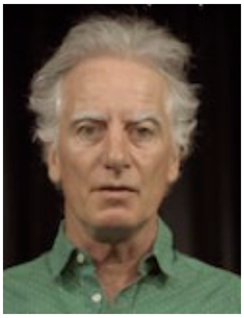

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Preface

It is a great honour for me to write these few lines of preface to the special issues of *Substantia* dedicated to the 150th anniversary of the Periodic Table by Dmitrij Mendeleev. In 2019 there are other important anniversaries besides that of the periodic table. One of these is the centenary of Primo Levi's birth. I believe these two anniversaries are strictly related, in fact *The Periodic Table* by Levi has been considered by the *Royal Institution of Great Britain* as the "best book of science ever written". It would be sufficient to recall an impressive excerpt from "Iron", a tale of the *The Periodic Table*, to acknowledge the uniqueness of this literary work:

> "*We began studying physics together, and Sandro was surprised when I tried to explain to him some of the ideas that at that time I was confusedly cultivating. That the nobility of Man, acquired in a hundred centuries of trial and error, lay in making himself the conqueror of matter, and that I had enrolled in chemistry because I wanted to remain faithful to this nobility. That conquering matter is to understand it, and understanding matter is necessary to understand the universe and ourselves: and that therefore Mendeleev's Periodic Table [...] was poetry ...*".

When we designed the project related to these special issues, we had in mind Levi's work and in particular his wonderful tales that belong to *The Periodic Table*. I like to recall this homage to a chemist-writer-witness to introduce the six topics that are associated to the special volumes of *Substantia*.

As President of the University of Florence which is the owner of the publisher *Firenze University Press*, I am truly grateful to the Editors – Marc Henry, Vincenzo Balzani, Seth Rasmussen, Luigi Campanella, Mary Virginia Orna with Marco Fontani, and Brigitte Van Tiggelen with Annette Lykknes and Luis Moreno-Martinez – for accepting the invitation made by the Editor-in-Chief Pierandrea Lo Nostro and for the extraordinary work for the preparation of these special issues. Of course the choice of the six subjects was not accidental: we tried to identify some features of the chemistry realm, related for several reasons to the periodic table. They are strikingly associated to the great challenges for our future: these are water, sustainability, energy, open chemistry, the history and the educational perspectives of the periodic table.

During its long path of progress and civilisation mankind has strongly modified nature to make our planet more comfortable, but at present we must be very careful with some dramatic changes that are occurring in our Earth. Science and technology, and chemistry primarily, can help mankind to solve most of the environmental and energy problems that emerge, to build a radically different approach from that that has prevailed in the last two centuries. It is a fantastic challenge, since for the first time we can consider nature not as a system to simply exploit, but a perfect ally for improving life conditions in the whole planet. Chemistry has already engaged and won a similar challenge when, understanding the pollution problems generated by a chaotic and rapid development, succeeded in setting up a new branch, green chemistry, that turned upside down several research topics. Now is the time to develop sustainable chemistry: the occurring events demand that chemists propose new routes and innovative approaches. In the last two centuries we have transformed immense amounts of matter from nature into waste without thinking that we were using non renewable energy sources. We have been acting as our natural resources were unlimited, but knowing that they are instead limited. Now we are realizing that it is not possible to continue along this road. Our planet and our atmosphere are made of finite materials and their consumption during the last two centuries has been impressive. Some elements that are crucial for current and future industrial countries are known to be present on Earth crust in very small amounts and their recycling from waste cannot be a choice anymore, but it is rather an obligation.

Climate is another big problem associated to the terrific changes occurring in some equilibria, both as a consequence of the violent industrial development and energy consumption. We need, and we will always need more and more, an immense amount of energy. The only solution to secure wellness to future generations is the conversion to renewable energy sources. In this view, food and water, due to the strong increment in the demographic indices, could become the true emergencies for billions of individuals. Looking at the picture I tried to draw in this short preface it becomes more clear why we selected those topics for our special issues.

I am optimistic, and I have the strong confidence that chemistry, that studies matter and its transformations, will give mankind the picklock to overcome those challenges.

We will definitely need insightful minds, creativity, knowledge and wisdom.

Luigi Dei
President of the University of Florence

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Editorial

Saving the planet and the human society: renewable energy, circular economy, sobriety

Vincenzo Balzani

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Abstract. Planet Earth is a very special spaceship that cannot land or dock anywhere for being refueled or repaired. We can only rely on the limited resources available on the spaceship and the energy coming from the Sun. The huge amounts of carbon dioxide produced by using fossil fuels in affluent countries has caused global warming, which is responsible for climate change. Ecological degradation of the planet is accompanied by an increased social disparity. As Pope Francis warns, we are faced with a complex crisis which is both social and environmental. Strategies for a solution demand an integrated approach to combating poverty and protecting nature. If we want to continue living on planet Earth, we must achieve the goals of ecological and social sustainability by implementing three transitions: from fossil fuels to renewable energies, from a linear to a circular economy, and from consumerism to sobriety. Science, but also consciousness, responsibility, compassion and care must be the roots of a new knowledge-based society.

Keywords. Sustainability, energy, materials, environment, climate crisis, social crisis, economy, efficiency, sobriety.

Scientist are called to see
what every one else has seen
and think what no one else
has thought before

1. LIVING ON SPACESHIP EARTH

The image taken by the Cassini Orbiter spacecraft on September 15, 2006, at a distance of 1.5 billion kilometers, shows the Earth as a pale blue dot in the cosmic dark (Figure 1). There is no evidence of being in a privileged position in the Universe, no sign of our imagined self-importance.

There is no hint that we can receive help from somewhere, no suggestion about places to which our species could migrate.

Like it or not, planet Earth, the only place we can live on, is a kind of spaceship that travels in the infinity of the Universe. It is a very special spaceship, however, because it cannot land or dock anywhere for being refueled or repaired. Any damage has to be fixed and any problem has to be solved by us passengers, without disembarking. We travel alone in the Universe, and we can only rely on the energy coming from the Sun and on the resources available in our spaceship.[1] The first thing we passengers should be aware of is that the planet Earth has "finite" dimensions. Therefore, the resources we have are limited and the space for waste disposal is also limited. This is an undeniable reality, even though many economists and politicians seem to ignore it.

The views from space have allowed us to observe the entire Earth as a planet. In the Earth-at-day images from the space, national boundaries are invisible and this may strengthen the consciousness of the collective human responsibility for the future of our planet. On the contrary, the Earth-at-night images show boundaries: those between affluent and poor areas. The passengers of spaceship Earth travel, indeed, in very different "classes". Disparity is the most worrying feature of our society. The number of billionaires has almost doubled, with a new billionaire created every two days between 2017 and 2018. They have now more wealth than ever before while almost half of humanity have barely escaped extreme poverty, living on less than $5.50 a day.[2]

Figure 1. Photograph taken by the Cassini Orbiter spacecraft on September 15, 2006, at a distance of 1.5 billion kilometers from Earth. The dot to the upper left of Saturn's rings, indicated by the arrow, is the Earth. Saturn was used to block the direct light from the Sun otherwise the Earth could not have been imaged.

In his encyclical letter Laudato si' Pope Francis warns:[3] "The pace of consumption, waste and environmental change has so stretched the planet's capacity that our contemporary lifestyle, unsustainable as it is, can only precipitate catastrophes (paragraph 161). He adds: "We are faced not with two separate crises, one environmental and the other social, but rather with one complex crisis which is both social and environmental. Strategies for a solution demand an integrated approach to combating poverty, restoring dignity to the excluded, and at the same time protecting nature" (paragraph 139).

If we want to continue living on Earth, we must achieve the goal of ecological and social sustainability by going through three transitions: from fossil fuels to renewable energies, from a linear to a circular economy, and from consumerism to sobriety.

2. FROM FOSSIL FUELS TO RENEWABLE ENERGIES

Energy is the most important resource for humanity[1]. In the present Anthropocene epoch[4], as primary energy we use mainly fossil fuels, a non-renewable resource that in the long run is going to be exhausted. In 2018, *every second* in the world we have burned 250 tons of coal, 1140 barrels of oil and 105,200 cubic meters of gas,[5] generating heat along with pollution and 1074 tons of carbon dioxide (CO_2).

That the use of fossil fuels generates substances that are harmful to health has always been known, but it was only in the mid-1980s that another, more serious, problem emerged: the enormous amounts of CO_2 released into the atmosphere cause global warming (greenhouse effect) which is responsible for climate change.[6]

Since 1992, several United Nations sponsored conferences tried to tackle the problem of climate change without success. In 2014 the 5th IPCC (*Intergovernmental Panel on Climate Change*) Assessment Report showed that the influence of human activities on climate change is unequivocal and increasingly worrying: the Earth warms up, glaciers melt, sea level rises, drought advances, extreme weather events are more and more frequent. In December 2015, after a long cycle of negotiations, the United Nations organized a conference in Paris, preceded by Pope Francis' encyclical *Laudato si'* in which climate change and related problems had been addressed with great authority and concern[3]. At the Paris Conference, 196 national delegations approved an agreement based on the following points: (i) it is absolutely neces-

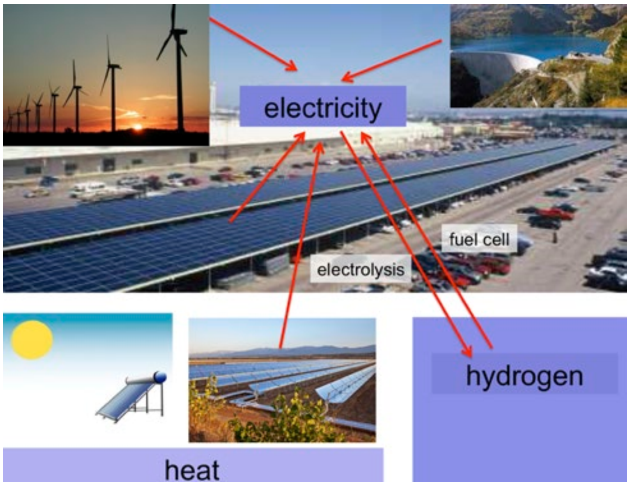

Figure 2. Renewable primary energies generate electricity.

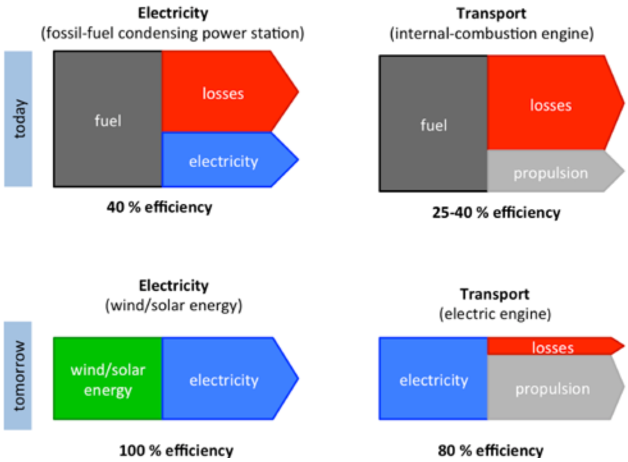

Figure 3. Conversion of primary energy (fossil fuels or wind/solar energy) into electricity and mechanical energy (adapted from[10]).

sary to reduce strongly, or better eliminate greenhouse gas emissions by 2050, to limit the increase in global average temperature to less than 2 ° C (possibly, less than 1.5 ° C) compared to the pre-industrial level; (ii) in tackling the problem of climate change, all countries must consider, respect and promote human rights; (iii) it is urgent that developed nations make financial and technological resources available to enable developing countries to reduce their greenhouse gas emissions.

Beyond the lack of concreteness of the commitments made, the Paris Agreement induced a strong cultural change. In spite of the withdrawal of the USA from the agreement, decided by President Trump in August 2017, there is a broad scientific and political consensus that the transition from fossil fuels to renewable energies will stop climate change, avoid the premature death of many people, increase the number of jobs, bring economic benefits and even advantages from the social point of view because the poorest nations, those most affected by climate change, are the richest in renewable energies[1]. However, at the Katowice conference in December 2018 it was verified that the energy transition proceeds too slowly and that the objectives of the Paris Agreement will not be achieved without a strong acceleration[6]. One of the most controversial problems about the transition concerns its costs/benefits, as thoroughly discussed with different opinions in two chapters of this issue.[7,8]

Renewable primary energies of the Sun, wind and water, that we should use to replace fossil fuels,[1] not only do not produce CO_2 and pollution, but they have the advantage of generating electricity instead of heat (Figure 2).

Electricity is the most valuable form of energy because it can be stored as chemical energy (batteries or hydrogen), used as such, or converted with high efficiency into mechanical energy (Figure 3).[9] Thus, the economy based on renewable energy sources is not only cleaner but also much more efficient than the fossil fuel based economy.

The energy transition from fossil fuels to renewable energy is proceeding. For example, at the end of 2018 the installed power was 505 GW and 591 GW for photovoltaic (PV) and wind energy, respectively.[11] At present PV is less developed than wind energy, but PV increases at a much faster rate (25% a year) and in 2050 it will become the most important source of energy for mankind. PV is indeed an ideal source of energy: it converts sunlight into electricity with 20% efficiency (100 times more than natural photosynthesis!), it can be used everywhere, it is scalable, long lasting, cheap and reliable. For some top research in the field of conversion of solar energy into electric energy, see.[12, 13]

The unavoidable transition from fossil fuels to renewable energies, however, is hindered not only by commercial competition, but even more by obscure interests of various kinds: military, because fossil fuels, with their high energy intensity, are not only the object of wars, but also the most important resource for fighting; national, because many countries have abundant reserves of fossil fuels and do not intend leaving them underground; financial, because speculation does not care about the health of the planet; economic, because in many countries oil companies have become so powerful as to condition government policy (this is what happens in Italy with ENI).

Therefore, all the people who care about our “common house”[3] should show a strong social and political commitment to accelerate the energy transition.

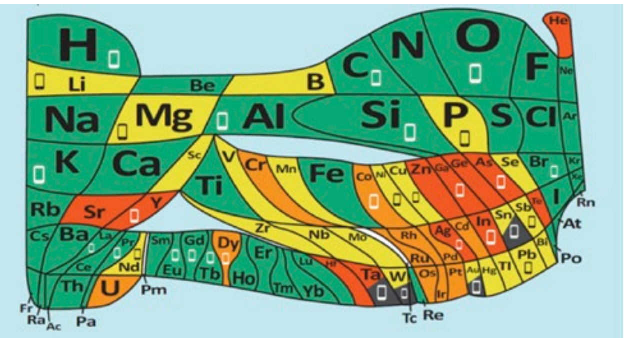

Figure 4. A "quantitative" Periodic Table [14].

3. THE MATERIALS PROBLEM

Since solar energy is abundant and can be converted with high efficiency, e.g. into electricity by PV modules, one could think that we are going towards an age of plentiful energy for every body.

This however, is not true because to exploit solar energy we need to construct equipment, machines and devices (e.g., PV cells), and to make them we must use materials available on the Earth. In the end, what we have on Earth are the chemical elements of the Periodic Table. Some elements are abundant, but others, including most of those needed for energy conversion, are scarce (Figure 4).

Therefore bottlenecks for the production of energy for final use are not the number of photons arriving from the sun or the availability of wind, but the materials we need for converting such primary renewable energies into the final energies that we use every day. Storage of the intermittent electricity generated by renewable energies is an important part of the problem.

Materials shortage affects several sectors of EU economy, in particular advanced technology.[15] The European Commission has compiled a list that contains 27 critical materials or classes of materials such as Platinum Group Metals or Rare Earth Elements.

Concern about criticity of some materials used for energy conversion and storage are based non only on shortage, but also on geographic, economic and political factors. For example, 95% of Rare Earth production comes from China and most of lithium, the basic component of the Lithium ion batteries used in ICT devices as well as electric vehicles, comes for Australia and Chile, and cobalt comes from a politically unstable country such as the Democratic Republic of Congo.[15]

4. FROM LINEAR TO CIRCULAR ECONOMY

As already underlined, Earth's resources are limited and the space available for waste disposal is also limited. Our current economic model however, the so called *Linear Economy* (Figure 5), is based on the assumptions that resources are infinite and that infinite is also the space for waste disposal: thus, we extract resources, use them to make products that then we throw away creating enormous amounts of waste that we think we can eliminate. All this by using energy from fossil fuels, which

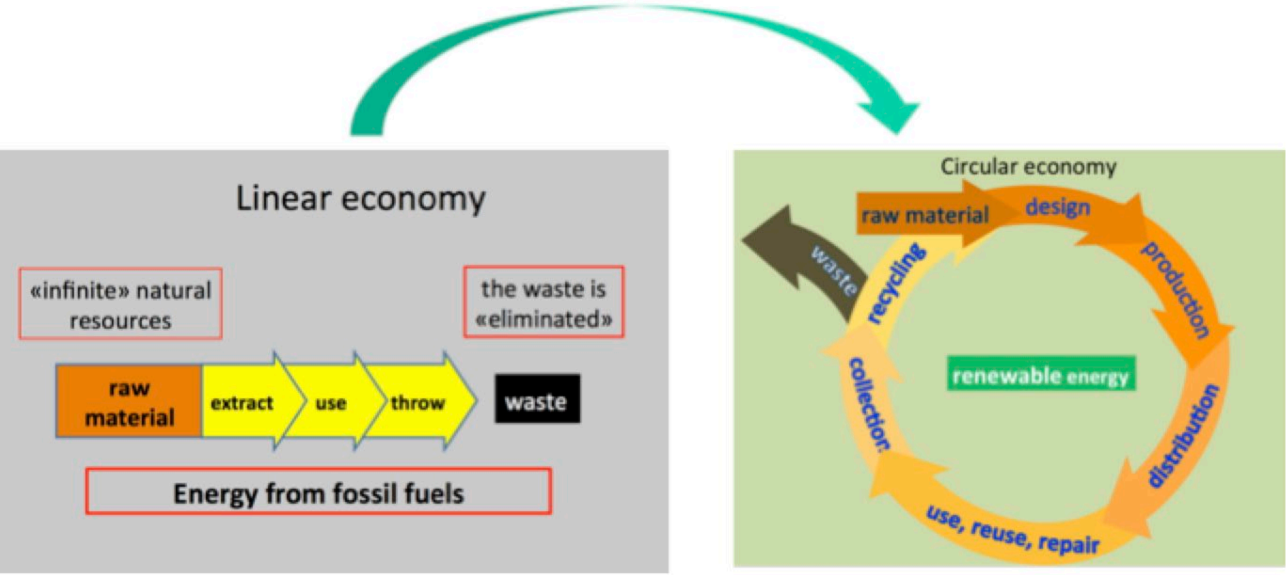

Figure 5. Schematic representation of the transition from a linear to a circular economy (adapted from[16]).

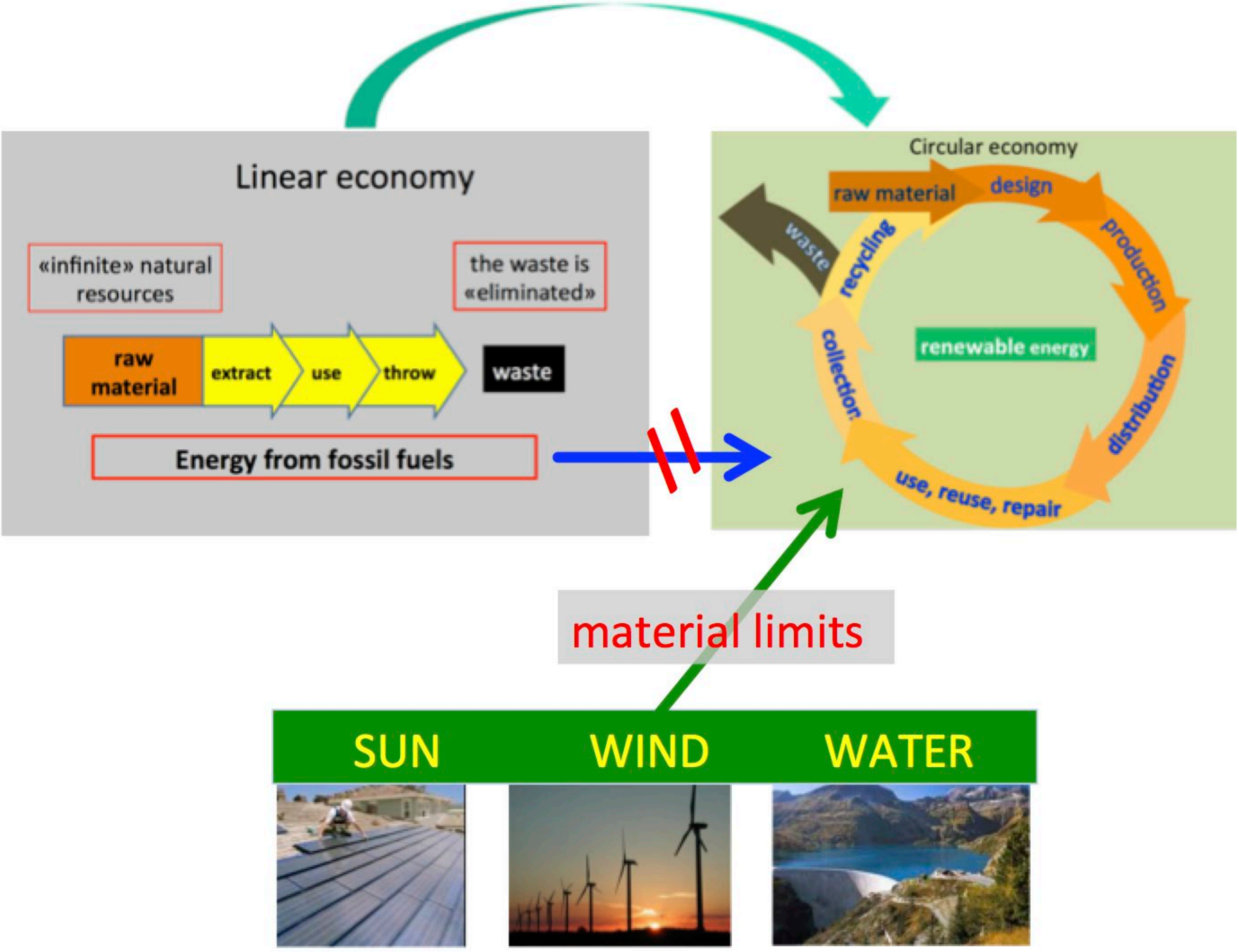

Figure 6. A circular economy system powered by renewable energies. The bottleneck is the avalability of materials for energy conversion (adapted from[16])

cause well known problems, including climate change. Such an economic model is clearly unsustainable.

We have to move to another economic model, the *Circular Economy* (Figure 5, right), which is based on the correct consideration that natural resources are limited. For this reason, raw materials must be used as little as possible (savings) and with high efficiency to fabricate things not only for use, but also for being repaired, reused, collected and recycled to provide new useful materials.

The only energy on which we can trust are renewable energies directly or indirectly related to sunlight (Figure 6). Therefore, more research should be devoted to improve energy conversion efficiencies and to develop means that can counter the two intrinsic defects of sunlight, low density and intermittency.

Can our civilization develop by adopting a circular economy powered by the electrical, mechanical and thermal energies obtained by the conversion of the primary, renewable energies of sun, wind and water? Perhaps not, if population continues to increase and everybody wishes to use more energy (and, in general, more resources), because of the bottleneck due to material limits (Figure 6). Therefore it could be wise to reduce our energy consumption, which poses a question: is it possible to live well using less energy and, more generally, less resources?

5. FROM CONSUMERISM TO SOBRIETY

The availability of energy is important for reaching a decent standard of life.[17,18] The average energy consumption of a United States citizen corresponds to about 7.0 toeq/year (toeq means tons of oil equivalent) or 9200 W, much more than the average energy consumption of a European citizen, about 3.2 toeq/year, or 4200 W. Data concerning the analysis of a series of parameters describing the quality of life (e.g., human development index, infant mortality) suggest that, at the current levels of efficiency in energy conversion, a primary consumption of around 2.6 toeq/year per person (about 3000-3500 W) can guarantee a good quality of life.[17,18] Therefore, all we citizens of affluent countries could decrease our energy consumption without losing our wellbeing. The same reasoning can be extended to any other resource we consume.

Interestingly, Swiss scientists have estimated that 2000 W (about 1,5 toeq/year per person) represents a sufficient amount of energy to live comfortably and the Swiss government has thus proposed a law to decrease to 2000 W the energy consumption per person (presently around 4700 W) by 2050-2100.[19] Such a law, in the form of a referendum, has been approved on May 21 2017 by Swiss citizens. Thus, for people living in rich nations reducing energy consumption is indeed possible without compromising the quality of life, which is good news.

A second question, however needs an answer: how can an affluent person reduce his/her energy consumption? Scientist involved in the study of this problem say that there are two routes. One is acting on "things", which means to increase the efficiency of all the devices and machines we use every day. For example, using more efficient cars, replacing fluorescent lamps with LEDs, increasing the thermal insulation of the house, etc. Experience shows, however, that increasing the efficiency of "things" often does not lead to a reduction in energy consumption for several reasons,[20] including the so called "rebound effect").[21] It may happen, indeed, that an increase in energy efficiency encourages a greater use of energy services. For example, when a person replaces an old car with a more efficient one (say a Euro 4 with a Euro 6) sometimes he is so proud to have bought a greener car that ends up using it more than the old one.

The other way to reduce energy consumption is acting on "people" rather than on things. We must start from the concepts of sufficiency and sobriety and "kindly" solicit[22] and, in extreme cases, oblige people, with laws and sanctions, to reduce unnecessary use of energyec services. To consume less, we have to "do less": fewer trips, less speed, less light, less heating, etc. If, after having adopted the strategy of sobriety, what we use is more efficient, we will have a even greater saving: it is doing less (sobriety) with less (efficiency).

What we have discussed above for energy also applies to any other type of resources. We need to change our lifestyle based on consumerism, that means *produce-sell-buy-use-throw* away regardless of the resource consumed, the real utility of the object made or service supplied, and the kind of waste generated. We need to enter a logic of sufficiency to attain ecological stability. We need to learn to say "enough".

6. CONCLUSION

Up until now we have taken from Nature any kind of resources to increase our well-being. Only a relatively small part of mankind, however, has made use of them, and it appears that there are insufficient natural resources to bring all people at the level of consumption of affluent countries. The claim for new goods and services is deeply entrenched in Western culture, which sees growth and development as absolutes. Indeed, in the Western world, the pressure made by ceaseless advertisements quickly converts goods and services, originally considered luxuries, into necessities for everyone. We are persuaded to consume at a faster and faster rate, without any understanding of the consequences of that consumption. The most pessimistic among scientists think that at the end we will be forced by the degradation of the planet to chose sobriety.

Indeed, only a new set of ethics and policies, accompanied by decisive changes in attitudes and practices can prevent a destructive collapse of the planet. We should take the energy and climate crisis as an opportunity to move away from fossil fuels, to reduce disparities, increase international cooperation, and lead humanity to an innovative concept of prosperity. Science, but also consciousness, responsibility, compassion and care must be the roots of a new knowledge-based society.

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Energy in a changing climate

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Abstract. Warming of the Earth's climate represents the "great challenge" of our times that may even undermine the subsistence of humankind on the planet. This paper reviews the causes and effects of climate change due to the anthropogenic activities. Since energy production constitutes the main source of climate-forcing anthropogenic emissions, a particular emphasis is given in the paper to the energy system transition to meet the objectives of the Paris Agreement, the international treaty signed in 2015 under the auspices of the United Nations Framework Convention on Climate Change, aimed at reducing the risks and effects of climate change on the global society.

Keywords. Climate change, anthropogenic emissions, energy system transition, IPCC, Paris agreement.

1. THE EARTH'S CLIMATE SYSTEM

The term "climate" (from the ancient Greek word *klima*: inclination) refers to the meteorological and environmental conditions in a given geographical area averaged over a long period of time, typically 30 years or more, as defined by the World Meteorological Organisation (WMO).

The Earth's climate system includes different components, sometimes referred to as "compartments", which interact dynamically with each other: atmosphere, ocean, Earth surface, cryosphere and biosphere, the life on the planet, including mankind. The system evolves with time, influenced both by an internal dynamics and by external factors called climate forcings. Climate forcing can either be due to natural phenomena (natural forcing) or to anthropogenic activities, in the latter case defined as anthropogenic forcing.

The "engine" of the Earth's climate is the Sun. The Earth's surface, in fact, receives energy from the Sun, 50% of which in the visible part of the electromagnetic spectrum. Part of the incident radiation is reflected back to space by the Earth's surface and by the clouds. The fraction of reflected energy is defined "albedo". The Earth's albedo is on average approximately 0.3 (30% of the solar energy is reflected back to space), but varies considerably in different areas of the globe depending on the nature of the surface: snow and ice, sea surface, vegetation, desert, urban areas, etc. To balance the absorbed incoming energy, the Earth must radiate the same amount of energy back to

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space. Because the Earth is much colder than the Sun, it radiates at much longer wavelengths, primarily in the infrared part of the spectrum. The Earth reaches therefore an equilibrium temperature where absorption and emission are balanced (Fig. 1).

But in the atmosphere are naturally present certain atmospheric constituents such as water vapour, carbon dioxide (CO_2), methane (CH_4) nitrous oxide (N_2O) and other compounds that absorb a significant fraction of the infrared radiation emitted by the Earth. The absorbed energy is then re-emitted in all directions thus contributing to the warming of the lower levels of the atmosphere causing the so-called (natural) greenhouse effect, in analogy with the heat trapping effect of the glass walls in a greenhouse illuminated by the Sun that increases the temperature of the air inside (Fig. 1). These absorbing species are therefore cumulatively called greenhouse gases (GHGs).

In the absence of an atmosphere the radiative equilibrium temperature of the Earth would be purely a function of the distance of the Earth from the Sun and of the surface albedo that is -18°C. But, as a consequence of the natural greenhouse effect, the average surface temperature of the Earth is ca. 15°C, 33°C higher than the radiative equilibrium temperature.

It is easy to understand that, in the absence of the natural greenhouse effect, the life on the planet would not have developed, at least not in the way we now experience.

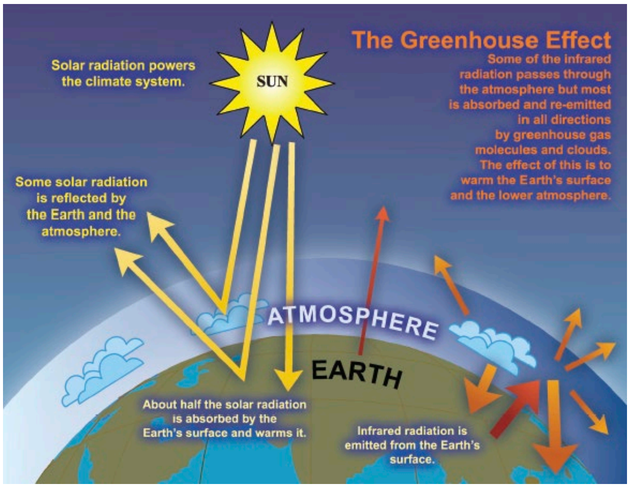


Figure 1. Schematic representation of the Earth's climate system and the greenhouse effect (from Le Treut et al., 2007).

2. THE ANTHROPOCENE

After the end of the last glaciation, ca. 12.000 years ago, the warmer temperatures caused by the natural greenhouse effect favoured, with the development of agriculture, the emergence of our civilization.

Since the onset of civilisation, man has modified the natural environment to make it more suitable to his needs, e.g. clearing large forested areas transformed into agricultural land. Until recent times, however, the world population was quite limited in number and the technologies available were relatively primitive, therefore the impact of humans on the environment had been quite limited both quantitatively and spatially.

But for the past two centuries or so the effects of humans on the global environment have increased dramatically. During the past two centuries, the human population has increased tenfold to more than 7 billion and is expected to reach 10 billions in this century. Humans exploit about 30 to 50% of the planet's land surface and use more than half of all accessible fresh water. Energy use has grown 16-fold during the twentieth century, causing 160 million tonnes of atmospheric sulphur dioxide (SO_2) emissions per year, more than twice the sum of its natural emissions. More nitrogen fertilizer is applied in agriculture than is fixed naturally in all terrestrial ecosystems; nitric oxide (NO) production by the burning of fossil fuel and biomass also overrides natural emissions. Fossil fuel burning and agriculture have caused substantial increases in the concentrations of GHG, CO_2 by 40% and CH_4 by more than 150%, reaching their highest levels over the past 800 millennia (Crutzen, 2002).

For all these reasons the Nobel Laureate Paul Crutzen and the biologist Eugene Stoermer suggested that the Holocene, the geologic epoch initiated with the end of the last glaciation has come to an end and that it seems appropriate to assign the term Anthropocene to the present geological epoch in many ways dominated by human activities (Crutzen and Stoermer, 2000).

There are different views concerning the beginning of the Anthropocene. While Crutzen and Stoermer had dated the beginning of the Anthropocene with the beginning of the industrial revolution in mid-18th century, Ruddimann (2013) has put forward the idea that mankind has started modifying the natural environment at least 9,000 years ago with the large deforestations to get cultivable land. Finally, more recent discussions have determined that the beginning of the Anthropocene as a geological epoch should be dated to the early 1950s, corresponding to the "Great Acceleration" after the 2nd World War, marked by a major expansion in human population, large changes in natural processes, the development of new materials and of the international trade (Lewis and Maslin, 2015).

3. CLIMATE CHANGE IN THE ANTHROPOCENE

Human activities contribute to climate change by causing changes in the atmosphere of the amounts of greenhouse gases and other gaseous and particulate components, with the largest contribution deriving from the burning of fossil fuels. Since the beginning of the industrial era, the overall effect of human activities on climate has been a warming influence and the human impact now greatly exceeds that due to natural processes, such as solar changes and volcanic eruptions (Forster et al., 2007).

The 5th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), published in 2014, reports that more than half of the observed increase in global average surface temperature from 1951 to 2010 was caused by the anthropogenic increase in GHG concentrations and other anthropogenic forcing agents together. In fact, the best estimate of the human-induced contribution to warming is similar to the observed warming over the same period (Fig. 2).

The observed surface temperature change in Fig. 2 is shown in black; the attributed warming ranges (colours) are based on observations combined with climate model simulations, in order to estimate the contribution of an individual external forcing to the observed warming. The 5 to 95% uncertainty range is superimposed to the bars.

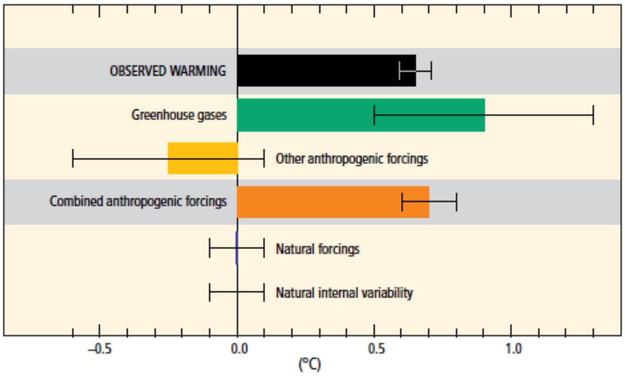


Figure 2. Comparison between the observed increase of global mean temperature (GMST) over the period 1951-2010 and the estimated anthropogenic contribution. The black bar is the observed GMST over the period, while the green and yellow bars represent the modelled contribution of GHGs and other climate forcers (mainly atmospheric aerosols that exert a cooling effect on climate; Fuzzi et al., 2015), respectively. The orange bar is the sum of the two (green + yellow) representing the total modelled temperature increase due to anthropogenic emissions. As can easily be seen, the modelled and observed GMST increase are very close to each other, taking into account the uncertainty ranges of the different quantities (the 5 to 95% uncertainty range is reported on top of each bar). The natural contributions to GMST increase and the internal variability of the Earth's climate system are minimal, if not negligible (from IPCC 2014).

Human-induced warming has now reached on average 1°C above pre-industrial levels in 2017, increasing at a rate of 0.2°C per decade, but warming greater than the global average has already been experienced in many regions and seasons (Allen et al., 2018).

3.1. Anthropogenic GHG emission

The main GHGs deriving from human activities are the above-mentioned CO_2, CH_4 and N_2O. These gases accumulate in the atmosphere, causing concentrations to increase with time. Significant increases of all these components have occurred in the industrial era (Fig. 3), with an even higher increase staring from the 1950s (the Great Acceleration). All of these increases are attributable to human activities (IPCC 2014).

Between 1750 and 2011, the cumulative anthropogenic CO_2 emissions to the atmosphere were 2040 ± 310 $GtCO_2$. About 40% of these emissions have remained in the atmosphere (880 ± 35 $GtCO_2$), the rest was removed from the atmosphere and stored on land (in plants and soils) and in the ocean that has absorbed about 30% of the emitted anthropogenic CO_2. What is more important, about half of the anthropogenic CO_2 emissions between 1750 and 2011 have occurred over the last 40 years.

CO_2 is not, as previously mentioned, the only GHG emitted by human activities, and Fig. 4 reports the glob-

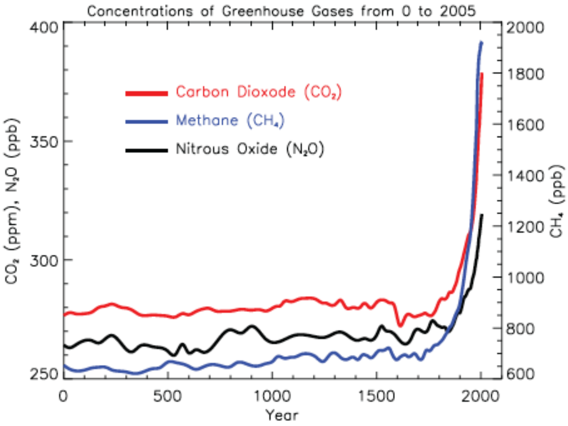


Figure 3. Atmospheric concentrations of the most important GHGs over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb) (from Forster et al., 2007). Present GHG concentrations (2017) are: CO_2 = 406 ppm, CH_4 = 1859 ppb, N_2O = 330 ppb (WMO, 2018).

al annual anthropogenic GHG emissions expressed as CO_2-equivalent (CO_2-eq). The global GHG emission in 2010 amounted to 49 Gt CO_2-eq.

The main drivers of anthropogenic GHG emissions are the population increase and the increasing energy needs of our society. Some figures illustrate the combined effects of the evolution of these two parameters.

At the time when agriculture emerged, about 10,000 B.C., the population of the world was estimated a few millions, growing to a couple of hundred millions by year 1 A.D.. Around 1800 the world population had reached one billion, with the second billion achieved in only 130 years (1930), the third billion in 30 years (1960), the fourth billion in 15 years (1974), and the fifth billion in only 13 years (1987). During the 20th century alone, the population in the world has grown from 1.65 billion to over 6 billions.

On the other hand, the world per-capita energy consumption, that amounted to some 20 GJ per year at the beginning of the 19th century has now reached ca. 80 GJ per year (Tverberg, 2012).

3.2. *Anthropogenic GHG emissions by economic sector*

All human activities cause the emission in the atmosphere of GHGs, and Fig. 5 reports the global anthropogenic GHG emissions from different economic sectors in 2010 (IPCC, 2014).

As can be seen from the figure, energy production constitutes the anthropogenic activity with the highest share of GHG emission (35%).

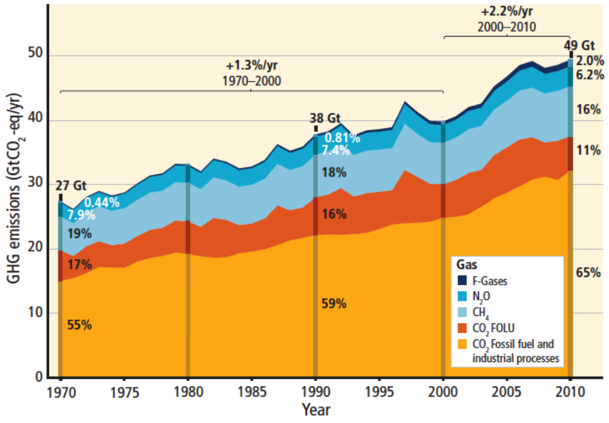


Figure 4. Total annual anthropogenic GHG emissions in gigatonnes of CO_2-equivalent per year ($GtCO_2$-eq/yr) for the period 1970 to 2010 by gases: CO_2 from fossil fuel combustion and industrial processes; CO_2 from Forestry and Other Land Use (FOLU); CH_4; N_2O; gases covered under the Kyoto Protocol (F-gases) (from IPCC, 2014).

4. THE EFFECTS OF CLIMATE WARMING

In recent decades, changes in climate have caused impacts on natural and human systems on all continents and across the oceans. The 5th IPCC Assessment Report has described in great detail the observed effects on the basis of some main climatic parameters (IPCC, 2014).

4.1. *Temperature increase*

Global warming (presently +1°C GMST with respect to the preindustrial period) is already negatively influencing the agricultural yields, thus affecting food security (Zhao et al., 2017). At the same time, the increase of seawater temperature is influencing the marine ecosystems and biodiversity. At present, the worldwide effect on human health of climate warming has been relatively small, although an increased heat-related mortality has been reported (e.g. the 2003 heat wave in central-southern Europe). Climate warming is also altering the precipitation regimes of several regions with effects on water availability and agricultural yields (Steffen et al., 2015).

4.2. *Sea level rise*

Over the period 1901–2010, global mean sea level rose by 0.19 m (0.17 to 0.21). This is mainly due to gla-

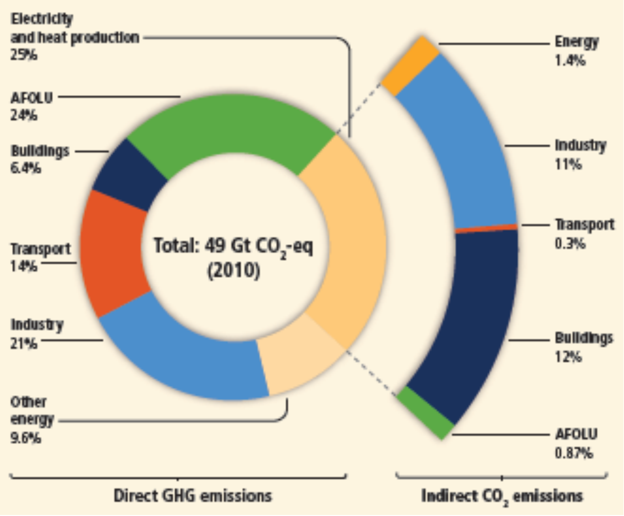


Figure 5. Total anthropogenic GHG emissions in $GtCO_2$-eq/yr) from different economic sectors in 2010. The circle shows the shares of direct GHG emissions in percentage of total emissions form the five main economic sectors. The pullout shows how shares of indirect CO_2 emissions from electricity and heat production are attributed to sectors of final energy use (IPCC, 2014).

cier mass loss and ocean thermal expansion (IPCC, 2014). The rate of sea level rise since the mid-19th century has been larger than the mean rate during the previous two millennia. Sea level rise is threatening all coastal areas with risk of flooding and the need of relocating the affected population (Nicholls et al., 2011).

4.3. *Melting of glaciers*

Over the last two decades, the Greenland and Antarctic ice sheets have been loosing mass and glaciers have continued to shrink almost worldwide, contributing on the one side to sea level rise, and on the other threatening freshwater availability in many regions of the world (IPCC, 2014).

4.4. *Extreme events*

The impact of recent climate-related extremes, such as heat waves, droughts, floods, cyclones and wildfires reveal significant vulnerability of some ecosystems and many human systems to current climate variability. Impacts of such climate-related extremes include alteration of ecosystems, disruption of food production and water supply, damage to infrastructures and other consequences for human wellbeing (IPCC, 2014).

5. THE PARIS AGREEMENT AND THE MEANS FOR THE IMPLEMENTATION

The policy actions to be implemented in order to limit the effects on the human society of the climate warming that is already happening fall under two broad categories:

- *mitigation* – measures aimed at reducing the emission of GHGs and other climate forcers (energy efficiency, decarbonisation, more efficient agricultural practices, etc.);
- *adaptation* – technological and infrastructural measures that allow contrasting the effects of climate change in progress.

Since more than 25 years the United Nations Framework Convention on Climate Change (UNFCCC) has been working on a global treaty that could reduce the GHGs emissions to contrast climate change. Finally, on December 12, 2015, within the 21st UNFCCC Session, 196 Countries, responsible for 95% of global GHG emission, approved the so called "Paris Agreement" that deals with GHG emissions mitigation, adaptation, and finance and that will formally start in the year 2020. The long-term overall goal of the Paris Agreement is to keep the increase in global average temperature to well below 2 °C above pre-industrial levels, and pursuing efforts to limit the temperature increase to 1.5 °C above pre-industrial levels, since this would substantially reduce the risks and effects of climate change.

IPCC was then invited by the UNFCCC to provide a Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways contained in the Paris Agreement. This Report was actually prepared and presented in October 2018 (IPCC, 2018).

The headline statements reported below from the Summary for Policymakers highlight some of the main conclusions of the report (IPCC, 2018). For a guide to the treatment of uncertainty within the IPCC reports, reference is made to Mastrandrea et al., (2010).

5.1. *Understanding global warming of 1.5°C*

Human activities are estimated to have caused approximately 1.0°C of global warming above pre-industrial levels, with a likely range of 0.8°C to 1.2°C. Global warming is likely to reach 1.5°C between 2030 and 2052 if it continues to increase at the current rate. (*high confidence*).

Warming from anthropogenic emissions from the pre-industrial period to the present will persist for centuries to millennia and will continue to cause further long-term changes in the climate system, such as sea level rise, with associated impacts (*high confidence*), but these emissions alone are unlikely to cause global warming of 1.5°C (*medium confidence*).

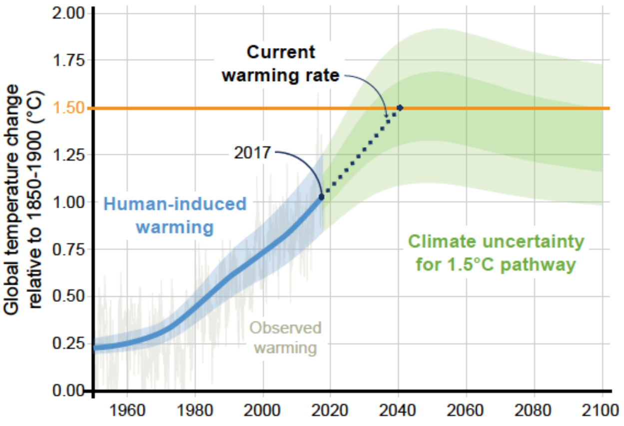


Figure 6. Human-induced warming reached approximately 1°C above pre-industrial levels in 2017. At the present rate, global temperatures would reach 1.5°C around 2040. Stylized 1.5°C pathway shown here involves emission reductions beginning immediately, and CO_2 emissions reaching zero by 2055 (from Allen et al., 2018).

Climate-related risks for natural and human systems are higher for global warming of 1.5°C than at present, but lower than at 2°C (*high confidence*). These risks depend on the magnitude and rate of warming, geographic location, levels of development and vulnerability, and on the choices and implementation of adaptation and mitigation options (*high confidence*).

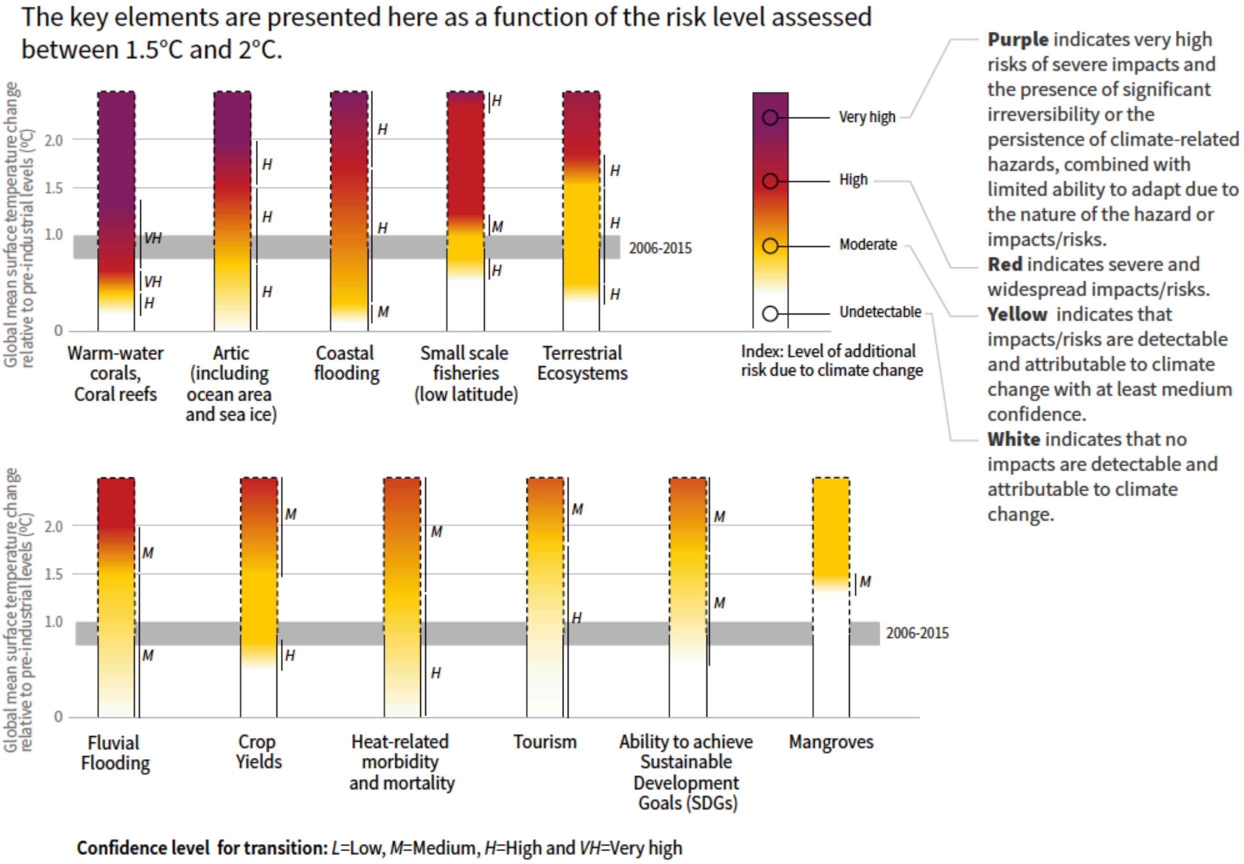
5.2. Projected climate change, potential impacts and associated risks

Climate models project robust differences in regional climate characteristics between present-day and global warming of 1.5°C, and between 1.5°C and 2°C. These differences include increases in: mean temperature in most land and ocean regions (*high confidence*), hot extremes in most inhabited regions (*high confidence*), heavy precipitation in several regions (*medium confidence*), and the probability of drought and precipitation deficits in some regions (*medium confidence*).

By 2100, global mean sea level rise is projected to be around 0.1 metre lower with global warming of 1.5°C compared to 2°C (*medium confidence*). Sea level will continue to rise well beyond 2100 (*high confidence*), and the magnitude and rate of this rise depend on future emission pathways. A slower rate of sea level rise enables greater opportunities for adaptation in the human and ecological systems of small islands, low-lying coastal areas and deltas (*medium confidence*).

On land, impacts on biodiversity and ecosystems, including species loss and extinction, are projected to be lower at 1.5°C of global warming compared to 2°C. Limiting global warming to 1.5°C compared to 2°C is projected to lower the impacts on terrestrial, freshwater and coastal ecosystems and to retain more of their services to humans (*high confidence*).

Limiting global warming to 1.5°C compared to 2°C is projected to reduce increases in ocean temperature as well as associated increases in ocean acidity and decreases in ocean oxygen levels (*high confidence*). Consequently, limiting global warming to 1.5°C is projected



Purple indicates very high risks of severe impacts and the presence of significant irreversibility or the persistence of climate-related hazards, combined with limited ability to adapt due to the nature of the hazard or impacts/risks.

Red indicates severe and widespread impacts/risks.

Yellow indicates that impacts/risks are detectable and attributable to climate change with at least medium confidence.

White indicates that no impacts are detectable and attributable to climate change.

Figure 7. The dependence of risks and/or impacts associated with selected elements of human and natural systems on the level of climate change, highlighting the nature of this dependence between 0°C and 2°C warming above pre-industrial level (from Hoegh-Guldberg et al., 2018).

to reduce risks to marine biodiversity, fisheries, and ecosystems, and their functions and services to humans, as illustrated by recent changes to Arctic sea ice and warm-water coral reef ecosystems (*high confidence*).

Climate-related risks to health, livelihoods, food security, water supply, human security, and economic growth are projected to increase with global warming of 1.5°C and increase further with 2°C. Most adaptation needs will be lower for global warming of 1.5°C compared to 2°C (*high confidence*). There is a wide range of adaptation options that can reduce the risks of climate change (*high confidence*). There are limits to adaptation and adaptive capacity for some human and natural systems at global warming of 1.5°C, with associated losses (*medium confidence*). The number and availability of adaptation options vary by sector (*medium confidence*).

5.3. Emission pathways and system transitions consistent with 1.5°C global warming

Two main pathways can be followed for limiting global temperature rise to 1.5°C above pre-industrial levels: i) stabilizing global temperature at 1.5°C or ii) global temperature temporarily exceeding 1.5°C before coming back down later in the century. In model pathways with no or limited overshoot of 1.5°C, global net anthropogenic CO_2 emissions decline by about 45% from 2010 levels by 2030 (40–60% interquartile range), reaching net zero around 2050 (2045–2055 interquartile range). For limiting global warming to below 2°C, CO_2 emissions are projected to decline by about 25% by 2030 in most pathways (10–30% interquartile range) and reach net zero around 2070 (2065–2080 interquartile range). Non-CO_2 emissions in pathways that limit global warming to 1.5°C show deep reductions that are similar to those in pathways limiting warming to 2°C (*high confidence*).

Pathways limiting global warming to 1.5°C with no or limited overshoot would require rapid and far-reaching transitions in energy, land, urban and infrastructure (including transport and buildings), and industrial systems (*high confidence*). These systems transitions are unprecedented in terms of scale, but not necessarily in terms of speed, and imply deep emissions reductions in all sectors, a wide portfolio of mitigation options and a significant up-scaling of investments in those options (*medium confidence*).

All pathways that limit global warming to 1.5°C with limited or no overshoot project the use of carbon dioxide removal (CDR) on the order of 100–1000 $GtCO_2$ over the 21st century. CDR would be used to compensate for residual emissions and, in most cases, achieve net negative emissions to return global warming to 1.5°C following a peak (*high confidence*). CDR deployment of several hundreds of $GtCO_2$ is subject to multiple feasibility and sustainability constraints (*high confidence*). Significant near-term emissions reductions and measures to lower energy and land demand can limit CDR deployment to a few hundred $GtCO_2$ without reliance on bioenergy with carbon capture and storage (BECCS) (*high confidence*).

6. ENERGY SYSTEM TRANSITION TO MEET THE OBJECTIVES OF THE PARIS AGREEMENTS

Realizing a 1.5°C-consistent pathway would require rapid and systemic changes on unprecedented scales in: i) the energy system, ii) land and ecosystem management, iii) urban and infrastructure planning, iv) the industrial system. As previously stated, the energy system constitutes the anthropogenic activity with the highest share of GHG emission and in this section mitigation and adaptation options related to the energy system transition will be reported, derived from the IPCC 1.5°C Report (de Coninck et al., 2018).

To limit warming to 1.5°C, mitigation would have to be large-scale and rapid. Transformative change can arise from growth in demand for a new product or market, such that it displaces an existing one. This is sometimes called “disruptive innovation”. For example, high demand for LED lighting is now making more energy-intensive, incandescent lighting near obsolete, with the support of policy action that spurred rapid industry innovation. Similarly, smart phones have become global in use within ten years. But electric cars, which were released around the same time, have not been adopted so quickly because the bigger, more connected transport and energy systems are harder to change. Renewable energy, especially solar and wind, is considered to be disruptive by some as it is rapidly being adopted and is transitioning faster than predicted. But its demand is not yet uniform. Urban systems that are moving towards transformation are coupling solar and wind with battery storage and electric vehicles in a more incremental transition, though this would still require changes in regulations, tax incentives, new standards, demonstration projects and education programmes to enable markets for this system to work (de Coninck et al., 2018).

Different types of transitions carry with them different associated costs and requirements for institutional or governmental support. Some are also easier to scale up than others, and some need more government support than others. The feasibility of adaptation and mitigation options requires careful consideration of multiple different factors. These factors include:

- whether sufficient natural systems and resources are available to support the various options (environmental feasibility);
- the degree to which the required technologies are developed and available (technological feasibility);
- the economic conditions and implications (economic feasibility);
- what are the implications for human behaviour and health (social/cultural feasibility);
- what type of institutional support would be needed, such as governance, institutional capacity and political support (institutional feasibility).

An additional factor (geophysical feasibility) addresses the capacity of physical systems to carry the option, for example, whether it is geophysically possible to implement large-scale afforestation consistent with the 1.5°C requirements (de Coninck et al., 2018).

6.1. Renewable energy

The largest growth driver for renewable energy has been the dramatic reduction in the cost of solar photovoltaic (PV). Solar PV with batteries has been cost effective in many rural and developing areas and small-scale distributed energy projects are being implemented in developed and developing cities where residential and commercial rooftops offer potential for consumers becoming producers (prosumers). The feasibility of renewable energy options depends to a large extent on geophysical characteristics of the area considered. However, technological advances and policy instruments make renewable energy options increasingly attractive in most regions of the globe. Another important factor affecting feasibility is public acceptance, in particular for wind energy and other large-scale renewable facilities that raise landscape management challenges, but financial participation and community engagement can be effective in mitigating resistance (de Coninck et al., 2018).

6.2. Bioenergy and biofuels

Bioenergy is renewable energy from biomass, while biofuel is biomass-based energy used in transport. There is high agreement that the sustainable bioenergy potential in 2050 would be restricted to around 100 EJ/yr. Sustainable deployment at higher levels, in fact, may put significant pressure on available land, food production and prices, preservation of ecosystems and biodiversity, and potential water and nutrient constraints. Some of the disagreement on the sustainable capacity for bioenergy stems from global versus local assessments. Global assessments may mask local dynamics that exacerbate negative impacts and shortages while, at the same time, niche contexts for deployment may avoid trade-offs and exploit co-benefits more effectively. The carbon intensity of bioenergy is still a matter of debate and depends on several factors such as management, direct and indirect land-use change emissions, feedstock considered and time frame, as well as the availability of coordinated policies and management to minimize negative side effects and trade-offs, particularly those around food security (de Coninck et al., 2018).

6.3. Nuclear Energy

The current deployment pace of nuclear energy is constrained by social acceptability in many countries due to concerns over risks of accidents and radioactive waste management. Though comparative risk assessment shows health risks are low per unit of electricity production and land requirement is lower than that of other power sources, the political processes triggered by societal concerns depend on the country-specific means of managing the political debates around technological choices and their environmental impacts. On the other hand, costs of nuclear power have increased over time and the current time lag between the decision date and the commissioning of plants is presently between 10 and 19 years (de Coninck et al., 2018).

6.4. Energy storage

The growth in electricity storage for renewables has been around grid flexibility resources. Battery storage has been the main growth feature in energy storage over the last few years mainly as a result of significant cost reductions due to mass production for electric vehicles. Although costs and technical maturity look increasingly positive, the feasibility of battery storage is challenged by concerns over the availability of resources and the environmental impacts of its production. Research and demonstration of energy storage in the form of thermal and chemical systems continues, but large-scale commercial systems are still rare. Renewably derived synthetic liquid (like methanol and ammonia) and gas (like methane and hydrogen) are increasingly seen as a feasible storage options for renewable energy, producing fuel for use in industry during times when solar and wind are abundant. The use of electric vehicles as a form of storage has also been evaluated as an opportunity, and demonstrations are emerging, but challenges to up-scaling remain (de Coninck et al., 2018).

7. CONCLUSION

Warming of the Earth's climate is a scientifically proven reality and represents the "great challenge" of our times that may even undermine the subsistence of our specie on the planet. Scientists have proven unequivocally that climate warming is already taking place and that human influence has been the dominant cause of the observed warming since the mid-20th century (IPCC 2014). It is then up to the policy makers to undertake the appropriate and timely actions for the mitigation of and the adaptation to climate warming that is already underway. In addition to political actions, citizen's behavioural attitudes are also important for mitigation of global warming: mobility choices, dietary habits, waste management, household management, etc..

It is also certain that several aspects of climate change will persist for centuries and that an effective endeavour for contrasting this phenomenon involves a commitment for many generations to come: higher emissions today imply the need of a higher decrease tomorrow, with higher economic and social costs.

Today, the global society has already available the scientific knowledge and most of the technologies needed to effectively contrast climate change, and the strategies to be put in place depend solely on political and economic choices. In any case, it should be considered that the social and economic costs of inaction towards climate change mitigation and adaptation are definitely higher than those for implementing the necessary mitigation and adaptation measures (Stern, 2007; Ricke et al., 2018).

ACKNOWLEDGEMENTS

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The Advent of Molecular Photovoltaics and Hybrid Perovskite Solar Cells

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Abstract. Over the past decade, we witnessed a remarkable development of a new generation of photovoltaic technologies, in particular dye-sensitized and perovskite solar cells. These systems have demonstrated potential to provide solutions for a more sustainable future in energy conversion. Both of these technologies, however, still encounter a number of challenges that stimulate further research. While dye-sensitized solar cells would benefit from an effective transfer from solution-based to a solid-state technology, hybrid perovskite solar cells suffer from long-term operational instability that need to be addressed. In this perspective article, we provide an overview of the recent advancements along with the perspectives for future developments.

Keywords. Molecular photovoltaics, dye-sensitized solar cells, perovskite solar cells, molecular modulation, layered hybrid perovskites.

1. INTRODUCTION

The increasing energy demands of our modern society and their impact on the environment call for novel solutions towards renewable energy conversion. One of the most auspicious technologies to meet these demands and prevent the devastating pollution caused by the combustion of fossil fuels are based on solar energy conversion.[1,2] Nature has long served as an inspiration in the ongoing quest for highly efficient light-harvesting technologies, stimulating research efforts towards sustainable energy. In natural photosynthesis, the control of molecular functions is often achieved through the role of supramolecular chemistry,[3,4] which involves fine-tuning of noncovalent interactions.[5-7] Such an approach inspired the development of a number of artificial molecular systems that convert external energy inputs into chemical energy.[5-7] In addition, natural photosynthesis has inspired the development of technologies for light-to-electrical energy conversion, in particular dye-sensitized solar cells (DSSCs).[8-12] In natural photosynthesis, the absorption of light triggers a sequential photoinduced electron transfer that contributes to the chemiosmotic gradient required to convert the electromagnetic stimuli into chemical energy that fuels the bioprocesses (Figure 1a).[3,4] Instead, in DSSCs an electrical potential gradient is generated via the photoinduced interfacial electron transfer from a molecular dye to a mesoscopic oxide, from where

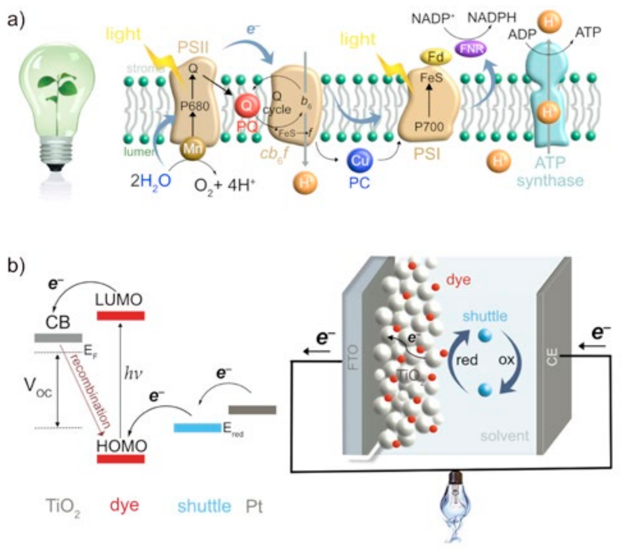

Figure 1. Schematic representation of the sequential electron transfer in (a) natural photosynthesis and (b) conventional dye-sensitized solar cells (pioneered by Grätzel at al.[8]) inspired by natural photosynthesis. PS = photosystem; ADP = adenosine diphosphate; ATP = adenosine triphosphate; NADP = nicotinamide adenine dinucleotide phosphate; NADPH = reduced NADP; Q = quinone; PQ = plastoquinone; PC = plastocyanin; P680 and P700 = chlorophyll pigments (P) of PSII and PSI, respectively, that best absorb light at either 680 nm or 700 nm, as indicated; Fd = ferredoxin; FNR = ferredoxin NADP reductase; CB = conduction band; LUMO = lowest occupied molecular orbital; HOMO = highest occupied molecular orbital; red = reduced; ox = oxidized.

it is extracted via a transparent contact to the external electric circuit. The complete cycle of converting light to electricity involves four key steps (Figure 1b): (1) photo-excitation of the light absorber (dye); (2) electron injection from the dye into the electron transport layer, commonly a mesoscopic TiO_2 or thin film transporting the charge carriers via the front contact into the external circuit; (3) dye regeneration by the redox shuttle that acts as an electron donor; and finally (4) shuttle regeneration at the counter electrode in the final step that closes the electric circuit.[10-12]

An effective solar-to-electric energy conversion requires alignment of the energy levels and favorable interaction of the participating species.[10-12] In a conventional DSSC, the redox mediator that "shuttles" electrons from the counter electrode to the photo-anode is dissolved in a liquid electrolyte. While this ascertains intimate contact with the sensitizer in the mesoporous film, it also poses limitations for industrial applications, thereby stimulating the development of solvent-free systems and solid-state technologies.[13-15] Therefore, the development of DSSCs using solvent-free ionic liquid electrolytes or solid-state hole conductors is of great interest.[13-15]

The advent of mesoscopic solar cells presented a new paradigm in photovoltaic technology as the electron- and hole-conducting materials form a three-dimensional junction, in contrast to the conventional planar p-n junctions. The prototype of this new photovoltaic family is the dye-sensitized solar cell (DSSC), also named the "Grätzel cell", which employs dye molecules, pigments or semiconductor quantum dots to sensitize a nanocrystalline wide bandgap semiconductor films. The landmark paper published in 1991 had a substantial impact being cited approximately 21'000 times until now.[8] According to an analysis by *Nature* in 2014, this publication ranks by number of citations amongst the top 100 papers of all time published across all domains of science. This revolutionary approach has allowed very high efficiencies to be reached in a photovoltaic conversion process that separated, for the first time, light harvesting and charge carrier transport, mimicking successfully the primary process in natural photosynthesis.

Ten years ago, the DSSC research became the cradle for the birth of a new closely related technology employing highly effective light absorbers known as hybrid organic-inorganic perovskites, which is referred to as perovskite solar cells (PSCs; Figure 2).[16-18] PSCs have emerged as the most promising thin-film, solution-processable, low-cost photovoltaic technology with extraordinary solar-to-electric power conversion efficiencies (PCEs) that have recently reached 25.2%, already surpassing the performance of the current market leader, polycrystalline silicon (Figure 2).[16,19-23] Unlike silicon, which is a material based on a covalent structural framework (Figure 2a),[24] hybrid perovskites are ionic crystals based on organic and inorganic components featuring mixed electronic-ionic conduction (Figure 2b).[19-26] These materials can be described by the AMX_3 formula, which is composed of a monovalent cation A (commonly methylammonium (MA) $CH_3NH_3^+$, formamidinium (FA) $CH(NH_2)_2^+$, guanidinium (GUA) $C(NH_2)_3^+$, and Cs^+), a divalent metal M (Pb_2^+, Sn_2^+), and a halide anion X (Cl^-, Br^-, I^-).[19-26] PSCs currently showing the highest performances are Pb-based comprising a mixture of different cations and halides.[22-26]

Despite their remarkable performance, however, the instability of PSCs against environmental factors, as well as under operational conditions, remains an issue that has to be addressed before practical applications become feasible (Figure 3).[27-30] This particularly refers to the sensitivity against oxygen and water, as well as heat and light stress (Figure 3a,c). Furthermore, significant effort is necessary to unravel the structure-property relationships and provide guidance for advanced material design for perovskites to reach a leading position in today's photovoltaics.[18,22]

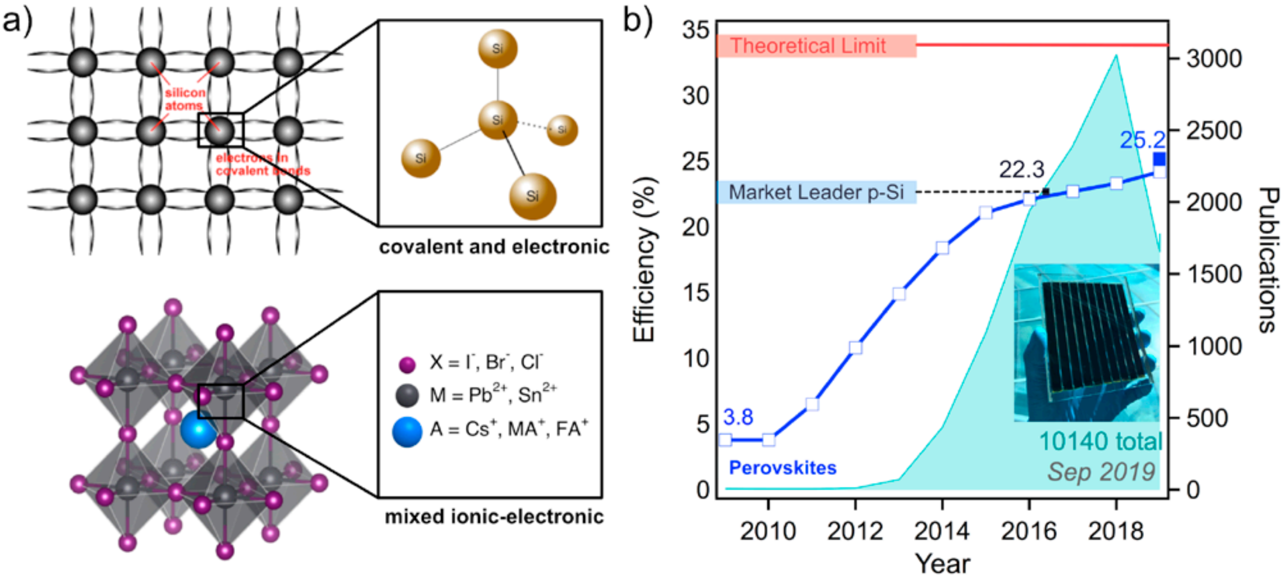

Figure 2. Structural representation of solar cell materials and the evolution of their performance. (a) Schematic representation of the structure of silicon (upper; figure adapted from ref.[24]) and hybrid perovskites (lower) with the chemical formula AMX_3. (b) Evolution of the photovoltaic performance of PSCs since 2009 (blue) in comparison to polycrystalline silicon (22.3% efficiency) and the theoretical limit (red), with the corresponding number of publications on hybrid perovskite solar cells (based on the Scopus analysis for the term "perovskite solar cell" on September 23, 2019). In 2019 the efficiency of PSCs has reached 25.2%.[16] A representative photo of a perovskite solar cell is shown in the inset (photo credit to the researchers at NTU Singapore).

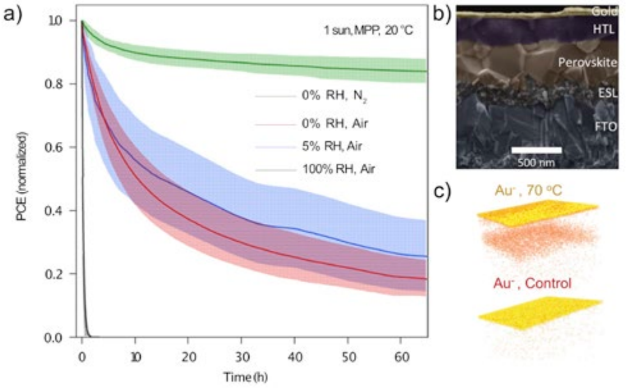

Figure 3. Aging of typical triple cation double halide perovskite solar cells. (a) Evolution of solar-to-electric power conversion efficiency under operational stability conditions upon continuous irradiation by maximum power point (MPP) tracking. Adapted with permission from ref.[30] (b) Cross-sectional scanning electron microscopy (SEM) image of a typical PSC highlighting its architecture and (c) time of flight secondary ion mass spectroscopy elemental depth profiling image showing the concentration of Au species across the device, indicative of ion migration under operational conditions at elevated temperatures. Adapted with permission from ref.[30] Copyright 2016 American Chemical Society.

In contrast to three-dimensional (3D) perovskites, their layered two-dimensional (2D) analogues have demonstrated promising environmental stability.[31-35] These materials are often described by the general $S_2A_{n-1}M_nX_{3n+1}$ formula. Here, species S (typically $C_mH_{2m+1}NH_3^+$) and A (typically MA, FA, or their mixtures) are organic cations, M is a divalent metal cation (Pb^{2+}, Sn^{2+}), X is a halide ion (Br^-, I^-), and the value n represents the number of layers of $[MX_6]^{4-}$ octahedra in the hybrid perovskite phase. The structure consists of layers of perovskite slabs separated by the organic ammonium cation spacers (Figure 4).[35] The spacer cation defines the properties of the layered 2D perovskites and consequently, the corresponding optoelectronic device performance.[36] The most commonly used spacers feature hydrophobic alkyl chains, such as *n*-buthylammonium (BA) or phenylethylammonium (PEA), which are essential to increasing the resilience of the material against the environmental factors. This contribution to the stability, however, comes at the expense of the solar-to-electric power conversion efficiency, which requires further advancement of these materials and the corresponding devices.[31]

2. RECENT ADVANCEMENTS OF DYE-SENSITIZED SOLAR CELLS

The inception of dye sensitized solar cells (DSSC) about 30 years ago by the Grätzel group provoked a revolution in photovoltaics.[8] He is credited with moving the

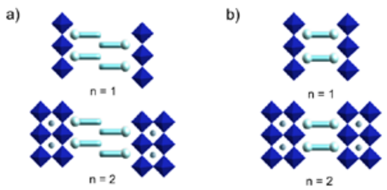

Figure 4. Structural representation of layered two-dimensional perovskites. Schematic of (a) $S_2A_{n-1}Pb_nI_{3n+1}$ (Ruddlesden-Popper, RP), (b) $SA_{n-1}Pb_nI_{3n+1}$ (Dion Jacobson, DJ) formulations with different number of inorganic layers (n). Blue octahedra illustrate the {PbI_6^{4-}} units, light blue spheres the A cations, whereas the cyan and green rods correspond to the organic spacers (S, S').

solar cell field beyond the principle of light absorption via diodes to the molecular level, exploiting the sensitization of wide bandgap semiconductor oxides by the dye molecules, pigments or semiconductor nanocrystals for light energy harvesting. The key to this success was the introduction of a new paradigm in photovoltaics. Instead of using the conventional planar p-n junction cell architecture, a 3D scaffold of semiconducting oxide nanoparticles was introduced in order to collect the electrons injected into the conduction band by the monolayer of adsorbed sensitizer molecules. The stacking of the nanoparticles produced a mesoscopic film with very high internal surface area, which enabled efficient light harvesting by the sensitizer. By contrast, on a flat surface, a self-assembled monolayer of molecular dye produces a very week photo-response, since the light absorption cross-section of a molecule is several orders of magnitude smaller than the area it occupies. Introducing a 3D mesoporous semiconducting oxide film as electron selective contact to support the sensitizer overcame this fundamental problem. As a result of its large internal surface area, the film achieves very efficient light harvesting even at monolayer surface coverage by dyes or semiconductor quantum dots. This, nevertheless, left the challenge to find a way to collect the electrons injected by the sensitizer into the nanoparticle network before they recombine with the positive charges left behind on the sensitizer. This task appeared to be particularly arduous in view of the fact that the charge carrier collection was not assisted by an electric field of the type present in a conventional planar p-n junction device.

Judicious molecular engineering of sensitizers enabled to address this challenge and to realize chromophores that would sustain the light-induced charge separation across the interface for long enough time to collect the photo-injected carriers before they were recaptured by the dye or by the oxidized form of the redox mediator. This development was supported by computational analysis, which provided precious help in the conception, design and synthesis of the best performing sensitizers.[37-41] Examples of some of the structures of the molecules that have emerged as some of the most powerful DSSC sensitizers and redox shuttles are shown in Figure 5. Due to their outstanding stability and broad visible light absorption, the bis-thiocyanato ruthenium bipyridyl complexes became the sensitizer of choice and are currently produced on the multi-kilogram scale for use in commercial products. The scaleup in production has lowered their prize by a factor of 100, from initially over 1000 US$/g to 10 US$/g, rendering DSSCs competitive with conventional systems. Today, we witness the emergence of organic and semiconductor quantum dots as sensitizers, which show superior light-harvesting properties to the ruthenium dyes. In-depth theoretical and experimental studies elucidated the fundamental features of the dynamics of interfacial electron transfer and charge carrier recombination within and at the surface of the semiconductor oxide nanocrystals. Laser photolysis in conjunction with time-resolved spectroscopy at the femtosecond time domain showed that judicious design of the sensitizer molecule allows to control the rate of the interfacial electron transfer reactions. For state-of-the-art sensitizers, the electron injection in the conduction band of TiO_2 scaffold occurs on the femtosecond to picosecond timescale, while the charge carrier recombination takes milliseconds or even seconds. This is sufficiently long to allow for near-quantitative collection of the photo-generated charge carriers as electric current. These molecular systems can generate photocurrents that were about 10'000- times larger than those obtained with planar architectures, converting over 90% of the incoming photons into the electric current within the absorption wavelength range of the sensitizer. The very efficient conversion of sunlight with molecular chromophores renders the DSSCs the first photovoltaic technology to mimic the light reaction in natural photosynthesis. This presents one of the most exciting developments in the generation of renewable energy from solar power.

A further advancement of DSSCs was made through the molecular engineering of a new donor-acceptor porphyrin sensitizer, coded YD2, achieving an efficiency record of 12.4 % when employed with a cobalt complex as redox shuttle (Figure 5).[42] Due to its beautiful green colour and its high efficiency, this sensitizer is presently upscaled for powering DSSC-based glazing (Figure 6). An example is the green sound protection barrier installed on the highway between Bern and Zurich that produces over 1000 kWh/year of electricity (Figure 6). Further computation-assisted molecular engineering of this type of donor-acceptor porphyrins allowed realizing panchromatic light harvesting across the whole visible spectrum, increasing the PCE to 13%.[43]

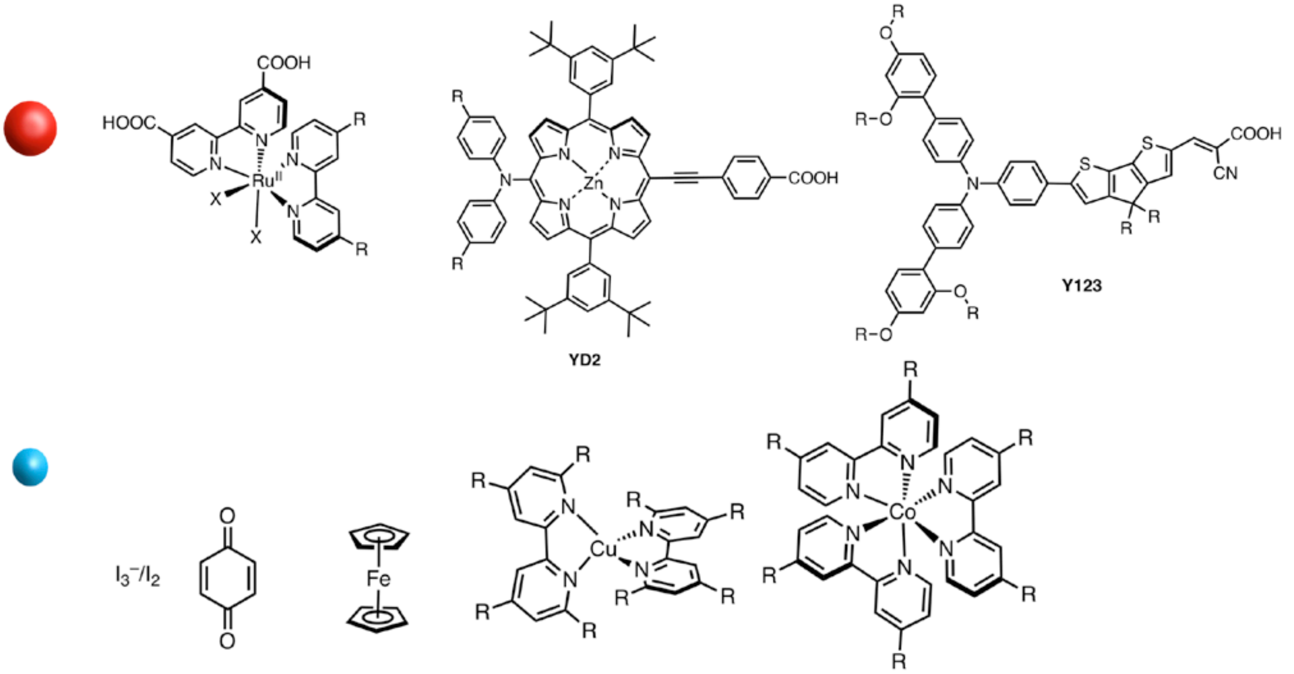

Figure 5. Structures of dye molecules (red) and redox shuttles (blue) commonly employed in DSSCs. Their roles are schematically illustrated in Figure 1b. R represents various alkyl/alkoxy substituents while X = SCN.

Ionic liquids played a crucial role as non-volatile, solvent-free redox electrolytes, enabling the practical deployment of DSSCs. New hydrophobic ionic liquids were developed displaying low viscosity, which have found widespread applications and are now produced commercially.[44] Substantial advances in performance were achieved by introducing eutectic mixtures of imidazolium iodide salts as redox active ionic liquids, where the charge transport is accelerated by a Groothus-type exchange mechanism.[45] The breakthroughs made in this area have dramatically increased the stability of DSSCs under prolonged light soaking and heat stress, fostering their practical development for outside deployment. Several companies are now manufacturing ionic liquid based on DSSCs on a commercial scale.

Solid-state dye sensitized solar cells are the main focus of current research efforts. Taking the inspiration from the work of C. Tang on organic light-emit-

Figure 6. Examples for DSSC-based photovoltaic glazing. Left: DSSC panels produced by the company Solaronix (www.solaronix.ch) mounted at the façade of the Swiss High-Tech Convention Centre in Lausanne, Switzerland. Right: The first energy-producing noise-barrier based on the DSSC panels developed by the Swiss company H.Glass is installed on the highway between Bern and Zurich in Switzerland.

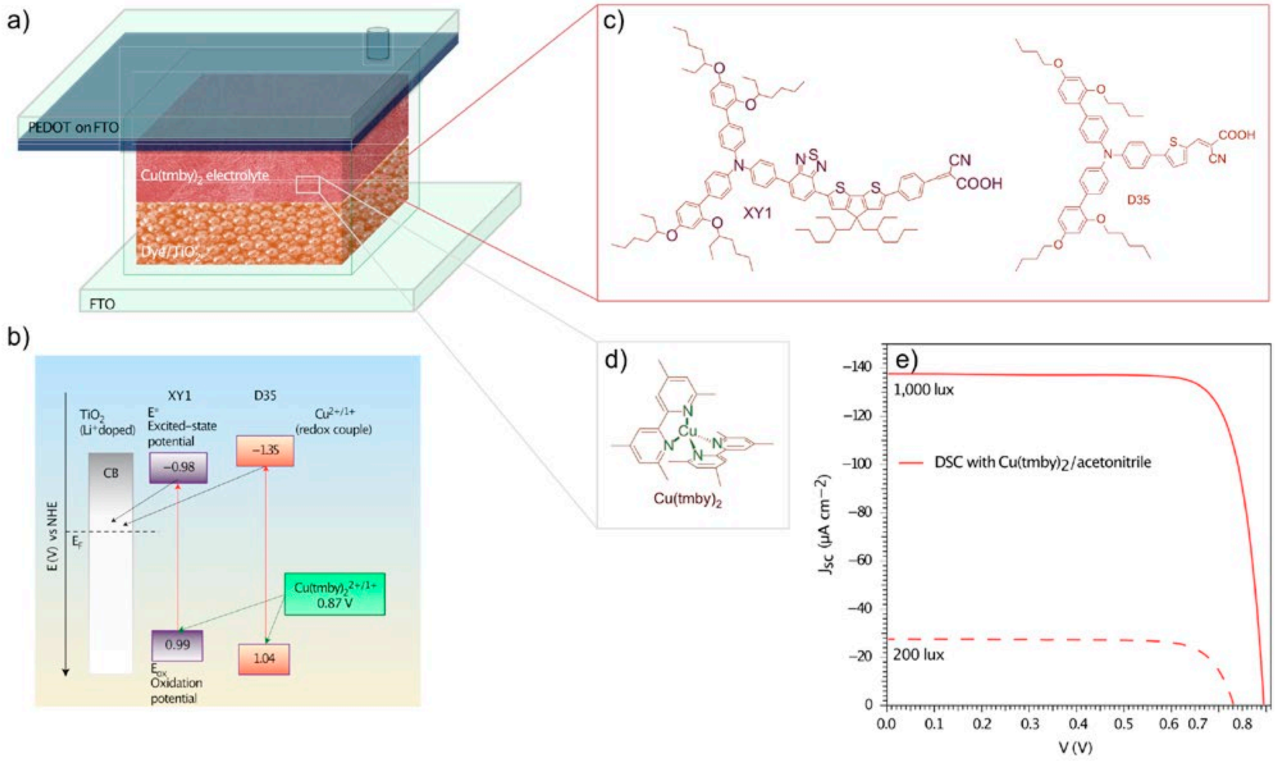

Figure 7. Example of a Cu-based dye-sensitized solar cell. (a) Schematic representation of the device architecture and (b) energy alignment of the device components, with the structure of the corresponding (c) dyes and (d) redox shuttle, as well as the (e) current-voltage characteristic at different light intensities. Adapted from ref.[47] with permission. tmby = 4,4',6,6'-tetramethyl-2,2'-bipyridine; PEDOT = poly(3,4-ethylenedioxythiophene); FTO = fluorine-doped tin oxide.

ting diodes, Grätzel et al. replaced the liquid electrolyte by solid organic hole conductors. Specifically, his group introduced the triarylamine derivative, namely 2,2',7,7'-tetrakis(*N,N*-di-pmethoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD), as a hole-transporting material, which is now widely applied.[46] Starting from low efficiencies below 1%, the PCE of solid-state DSSCs reaches presently over 11% using a solid-state Cu(II)/Cu(I) redox system for hole conduction. The advantage of employing a solid-state hole conductor is that it is non-volatile, showing faster charge carrier transport, while chemically less aggressive than a redox electrolyte. Hence, further research on solid-state DSSCs is presently being actively pursued. This development served as a springboard for the recent stunning rise of perovskite solar cells using the mesoscopic architecture of solid-state DSSC and hole conductors based on the spiro-MeOTAD family.

DSSCs based on Cu complexes as redox shuttles have taken the lead in electric power generation from ambient lighting.[47] Ambient light-harvesting systems are of great practical interest, as they can serve as electric power sources for portable electronics and can render the operation of a great variety of devices for wireless sensor networks (WSN) or IoT (Internet of Things) autonomous. A new DSSC embodiment has recently been shown to achieve high power conversion efficiencies (PCE) under ambient light conditions (Figure 7a,b). The photosystem combines two judiciously designed sensitizers coded D35 and XY1 (Figure 7c), with the copper complex Cu(II/I)(tmby) as redox shuttle (tmby = 4,4',6,6'- tetramethyl-2,2'-bipyridine; Figure 7d), which quantitatively regenerates both dyes at a very low driving force, resulting in open circuit photovoltages (V_{OC}) up to 1.1 V (Figure 7e). The electric power production at 1000 lux exceeded the PCE of GaAs under similar conditions, highlighting the potential of this technology.

3. RECENT ADVANCEMENTS OF HYBRID PEROVSKITE SOLAR CELLS

Since the first demonstration of the hybrid perovskite solar cell in 2009 by Miyasaka et al., the performance of this technology has rapidly evolved from

PCE of 3.8% to over 25% in just a decade, which has been unprecedented in photovoltaics (Figure 2b).[16,18,23,48] While this progress has been remarkable, PSCs continue to face obstacles to their application, which are mainly related to their instability against moisture and oxygen, as well as light and heat stress under operational conditions.[48,49] In addition, the progress in hybrid perovskite research has been primarily driven by the device performance, while the underlying degradation mechanisms and structure-property relationships remain poorly understood, which prevents rational material design required for further advancement.[48,49] To overcome these challenges, a number of strategies emerged over the past years with promising future prospects. Amongst these, three strategies related to the material design are particularly important (Figure 8), namely (1) compositional engineering, (2) employing a variety of modulators to the perovskite composition to alter their properties[50,51] as well as (3) layered two-dimensional perovskites and their heterostructures.[52,53] This progress was accompanied by the development of the analytical tools based on solid-state nuclear magnetic resonance (NMR) spectroscopy to unravel the structural properties at the atomic level and guide rational material design.[54-59]

Compositional engineering played a pivotal role in advancing PSCs since the properties of hybrid organic-inorganic halide perovskite materials are strongly dependent on their composition. This progress was facilitated by several major advancements. Following the first attempts to employ hybrid perovskite materials based on methylammonium (MA) cation,[60] Eperon et. al.[61] introduced the formamidinium (FA) to reduce the band gap from 1.53 eV to 1.48 eV and consequently increase the theoretical performance limit. However, the performance of FA-based compositions were lower than that of MA-based ones, since the perovskite-type $FAPbI_3$ polymorph (α-$FAPbI_3$) is not thermodynamically stable at temperatures below 150 °C and it transforms into the yellow polymorph (δ-$FAPbI_3$) under ambient conditions.[62] Phase stability of the mixed FA/MA compositions were improved by gradually substituting MA with FA cations,[19] and the utility of FA-based systems was further stimulated by their enhanced stability at elevated temperatures.[63,64] This approach of mixing cations in hybrid perovskites was advanced further by introducing 15% $MAPbBr_3$ in $FAPbI_3$ to reach PCEs above 18%.[65] Furthermore, Cs^+ was introduced into the composition to define the commonly employed triple cation $Cs_{0.05}MA_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})_3$ perovskite formulation, which provided a more reproducible and stable composition for PSCs reaching PCE beyond 21%,[25] and later on beyond 22% by reducing the bromide concentration.[17] Further progress in achieving the efficiencies that exceed 23% was reached through interfacial engineering[66] and by

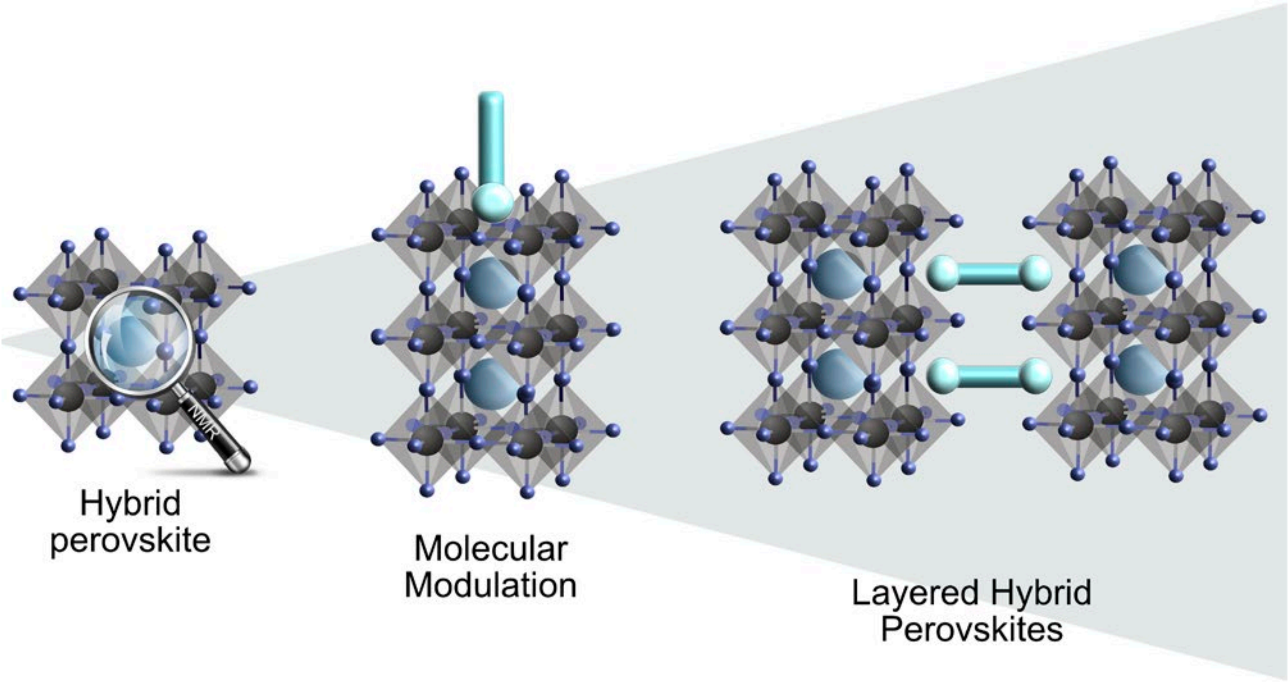

Figure 8. Gradual evolution of hybrid perovskite materials. Schematic representation of development through compositional engineering and molecular modulation to the layered hybrid perovskite materials.

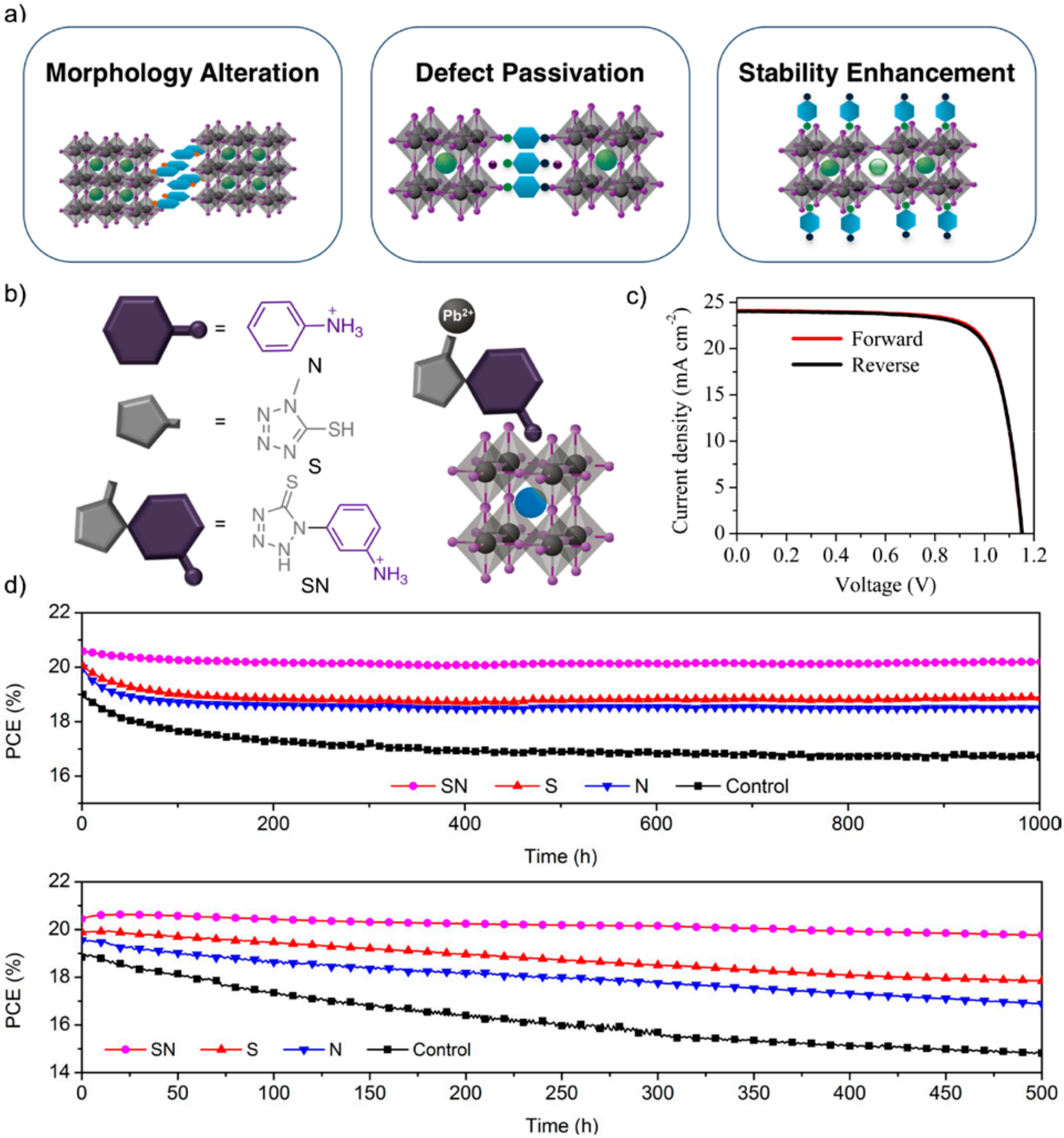

Figure 9. Molecular modulation case. (a) Overview of effects of molecular modulation on hybrid perovskite solar cells: morphology alteration, defect passivation, and stability enhancement. Adopted with permission from ref.[51] (b) Example of molecular modulators **N** (purple), **S** (grey), and **SN** (purple-grey) with a schematic representation of the interaction of **SN** with Pb^{2+} ions (grey sphere) and the hybrid perovskite ($FAPbI_3$). (c) *J-V* curves of the modulated champion device recorded in reverse (black; from V_{OC} to J_{SC}) and forward (red; from J_{SC} to V_{OC}) scanning directions under AM 1.5G solar radiation. (d) Evolution of power conversion efficiency of devices over time upon continuous light illumination at 65 °C and maximum power point tracking under argon (upper) and ambient air (lower) conditions. Adapted from ref.[76]

employing either molecular modulation or layered two-dimensional hybrid perovskite heterostructures.[67]

Molecular modulation refers to utilising organic molecules within the hybrid perovskite composition with the aim of addressing a specific function at the molecular level.[51] Three functional areas are particularly relevant for molecular modulation (Figure 9a), namely morphology alteration,[68-70] passivation of defects that might act as recombination centers,[71-73] and stabilization of the perovskite structure against the environmental factors as well as by suppression of the internal ion migration.[74,75] Milic and Grätzel et al. have shown that addressing these functional areas requires strategies that are based on purposefully tuning a variety of noncovalent interactions that can be employed to alter the morphology, passivate the defects, as well as self-assemble layers for either encapsulation or suppressing the detrimental ion migration.[51] For instance, a bifunctional modulator, 3-(5-mercapto-1*H*-tetrazol-1-yl)benzenaminium iodide (**SN**), was developed comprising of the anilinium core (**N**; purple in Figure 9b) that act as a hydrogen-bond-donating group for interaction with the surface of the hybrid perovskite and a thiol-tetrazolium unit (**S**; grey in Figure 9b) to coordinate the Pb^{2+} cations that can act as recombination centres.[76] These functional groups are used as part of a hydrophobic aromatic scaffold introduced with the objective of enhancing the tolerance to environmental factors. As a result, adding the modulator to the perovskite precursor solution and treating the surface of the thin films provided a beneficial effect on the optoelectronic properties. This was evidenced in photovoltaic devices of conventional mesoscopic Au/spiro-OMeTAD/perovskite/mesoporous-TiO_2/compact-TiO_2/fluorine-doped tin oxide (FTO) architecture, which were measured under conditions of standard AM 1.5G illumination at light intensity of 100 mW cm^{-2} (Figure 9c–d). The devices demonstrated an improvement of the photovoltaic performance as compared to the pristine (control) samples, including an increase of the short circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and the PCE (Figure 9 c–da). The J_{SC} improvements are ascribed to the higher electronic quality of the films and effective charge collection, whereas increased V_{OC} stems from the suppression of charge carrier recombination upon defect passivation.[51] This resulted in PCEs exceeding 20% PCE, with J_{SC} of 24 mA cm^{-2}, V_{OC} 1.15 V, and FF up to 0.75 (Figure 9c) for double cation single halide perovskite-based devices. Moreover, the exceptional performance was accompanied by a long-term stability upon continuous illumination at elevated degradation conditions between 55–60 °C in either argon atmosphere or humid ambient air (Figure 9d).[76] This enhancement in stability and performance upon modulation corroborates the suppression of morphological changes upon aging, as well as passivation of defects, in addition to an increase in hydrophobicity that was evidenced by contact angle measurements.[76]

Such effects of the modulation on the properties of hybrid perovskites are not limited to this modulator or a single perovskite composition.[51] The atomic-level interactions responsible for this function can be analysed by solid-state NMR spectroscopy, which sets the basis for advanced molecular design.

Solid state NMR spectroscopy is a powerful technique that provides atomic-level information about the microstructure of the material. It has been successfully employed to scrutinize the incorporation of the variety of organic and inorganic cations into the hybrid perovskite structure.[54-57] In particular, the comparison of ^{13}C, ^{14}N, and ^{15}N magic angle spinning (MAS) NMR spectra of neat mechanochemical α-$FAPbI_3$ and bulk mixtures with sub-stoichiometric amounts of modulators provide unique structural insights.[54-58] This involves identifying the interaction between the modulator and the hybrid perovskite, assessing whether it involves incorporation of the modulator insight the A cation site, as well as whether the interaction induces any changes in the perovskite crystallographic properties (Figure 10).

The interaction between the modulator and the perovskite can be evidenced by the appearance of new NMR resonances in the mixtures prepared mechanochemically.[51,76] For instance, a comparison between the ^{13}C NMR spectra of the **SN**-modulated α-$FAPbI_3$ perovskite (Figure 10a) and the neat modulator (Figure 10b) reveals a set of additional carbon environments, which can be associated with the **SN** interacting with the perovskite. The chemical shifts can also provide more information about the interaction and scrutinize the propensity of the modulator to incorporate into the corresponding A cation sites. In this regard, the ^{13}C and ^{15}N NMR spectra of the neat and **SN**-modulated α-$FAPbI_3$ material reveals similar ^{13}C and ^{15}N resonances (Figure 10c,d and Figure 10e,f), which suggests that **SN** does not incorporate into the perovskite lattice. However, a small (0.2 ppm) in the NMR spectra upon modulation evidences structural differences between the two materials, which points at the interaction taking place on the surface of the hybrid perovskite instead. Such interaction can result in the changes in the crystallographic properties of the hybrid perovskite, which can be uniquely probed by ^{14}N NMR spectroscopy. This is due to the dependence of the breadth of the residual ^{14}N spinning sideband (SSB) manifolds on the reorientation of FA inside the cuboctahedral cavity that is related to the symmetry of cation reorientation. Specifically, narrower ^{14}N SSB manifolds correspond to higher symmetry that is closer to cubic.[54] The ^{14}N MAS NMR spectra of neat (Figure 10g,i) and modulated α-$FAPbI_3$ (Figure 10h,j) show a SBB pattern that becomes narrower in the modulated material. This means that the modulation of α-$FAPbI_3$ phase increases its crystallographic symmetry,

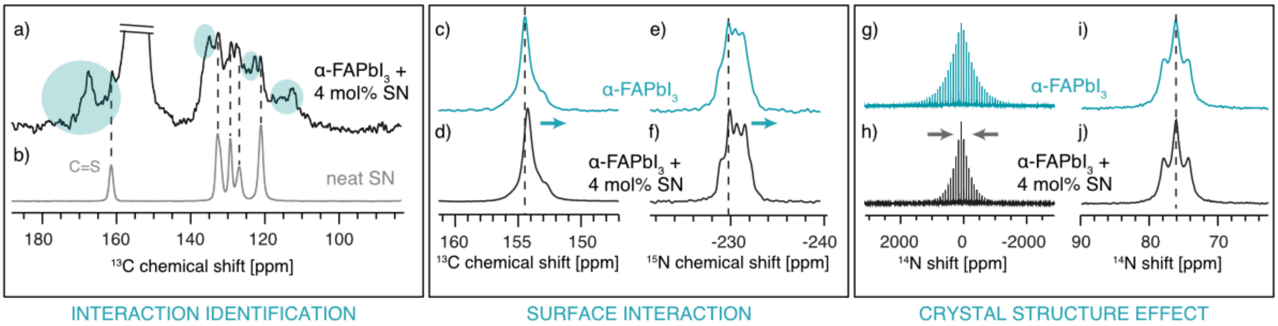

Figure 10. Probing molecular modulation at the atomic level by solid-state NMR spectroscopy. (a–b) Identifying interactions via ^{13}C cross-polarization (CP) solid-state magic angle spinning (MAS) NMR spectra at 11.7 T, 105 K, 10 kHz MAS of a) neat mechanochemical α-FAPbI$_3$ with 4 mol% **SN** and b) neat SN. Blue circles showcase the new environments that are associated with the interaction of the modulator. (c–f) Minor changes in the chemical shift (0.2 ppm) highlighted by the blue arrows of the ^{13}C CP and ^{15}N CP solid-state MAS NMR spectra at 11.7 T, 105 K, 10 kHz MAS of neat mechanochemical c,d) α-FAPbI$_3$ and e,f) α-FAPbI$_3$ with 4 mol% **SN** suggest that the interaction takes place on the surface of the hybrid perovskite as opposed to by A-cation incorporation. (g–j) Changes in the crystal structure of FAPbI$_3$ revealed by ^{14}N solid-state MAS NMR spectra at 11.7 T, 298 K and g,h) 3 kHz and i,j) 20 kHz MAS of bulk mechanochemical g) α-FAPbI$_3$ and h) α-FAPbI$_3$ with 4 mol% SN implied by narrowing of the SBB manifold (grey arrows). Panels i,j) shows the views of the center band. Adapted from ref.[51,76]

rendering it closer to cubic. Moreover, the peak features the same shift in both samples, which supports the conclusion that the change is not caused by incorporation of the modulator into the A cation site but rather a result of a surface interaction.[51,76]

Similarly, the interaction of the modulators with the potential defects, such as PbI$_2$, can be probed, which can serve to unravel the likelihood of defect passivation. This role of molecular modulators in directing the structure of hybrid perovskites and passivating some of the defects was found to benefit the device performance and stability even for the substoichiometric amounts of the modulator. Such molecular-level engineering assessed by solid-state NMR spectroscopy sets the stage for more elaborate material design with further enhanced stability, such as in the layered hybrid perovskites.

Layered hybrid perovskites fully incorporate the organic component within the layers of hybrid perovskite slabs. Following the pioneering work of Mitzi et al.[77] a number of layered perovskite materials were developed over the past years. While these systems can stabilize the perovskite structure, particularly against the detrimental effect of humidity, the performances of the resulting solar cells remain inferior to those of their 3D analogues. This can be attributed to the charge transport inhibition by the organic cations that act as insulating layers, since the inorganic domains mainly contribute to the electronic charge transport.[52,53] Moreover, they feature a larger exciton binding energy that results in the decrease of the performance that is often related to the short circuit current losses owing to inefficient exciton dissociation.[35] This can be circumvented by tuning the organic cation groups[35] or by employing hot-casting fabrication techniques.[31] A unique advantage of tunability of the properties based on the molecular design of organic spacer cations permits to rely on hydrophobic chains and van der Waals interactions between the adjacent layers to contribute to the stability, without compromising the crystallinity of the material.[32] Commonly employed organic cations, such as the BA or PEA, which form Ruddlesden-Popper perovskite phases, feature long alkyl chains that jeopardize the crystallinity of the materials.[35,36] Further engineering of the noncovalent interactions within the spacer layer has the propensity to boost the performances of this category of perovskites and the supramolecular strategies are underutilized in this context.

In order to demonstrate the potential for exploiting the Van der Walls interactions of the spacer layer, for instance, A$_2$FA$_{n-1}$Pb$_n$I$_{3n+1}$ (n = 1–4) compositions based on the (adamantan-1-yl)methanammonium (A) as a spacer were developed (Figure 11). Adamantane is a well-known building block in supramolecular chemistry that features ordered self-assembled structures based on Van der Waals interactions.[78-83] In addition, the high symmetry and dynamics of functional adamantane systems is known to be used in plastic crystals and molecular machines.[84] The utility of these systems was probed in the A$_2$FA$_{n-1}$Pb$_n$I$_{3n+1}$ formulations based on thermally stable FA-based perovskite compositions by using stoichiometries with different numbers of layers (n = 1 – 4) separated by the spacer. The unique property of layered 2D perovskites is that they behave as natural quantum wells that feature a gradual decrease in the bandgap (E_g) with an increase in the number (n) of inorganic layers,

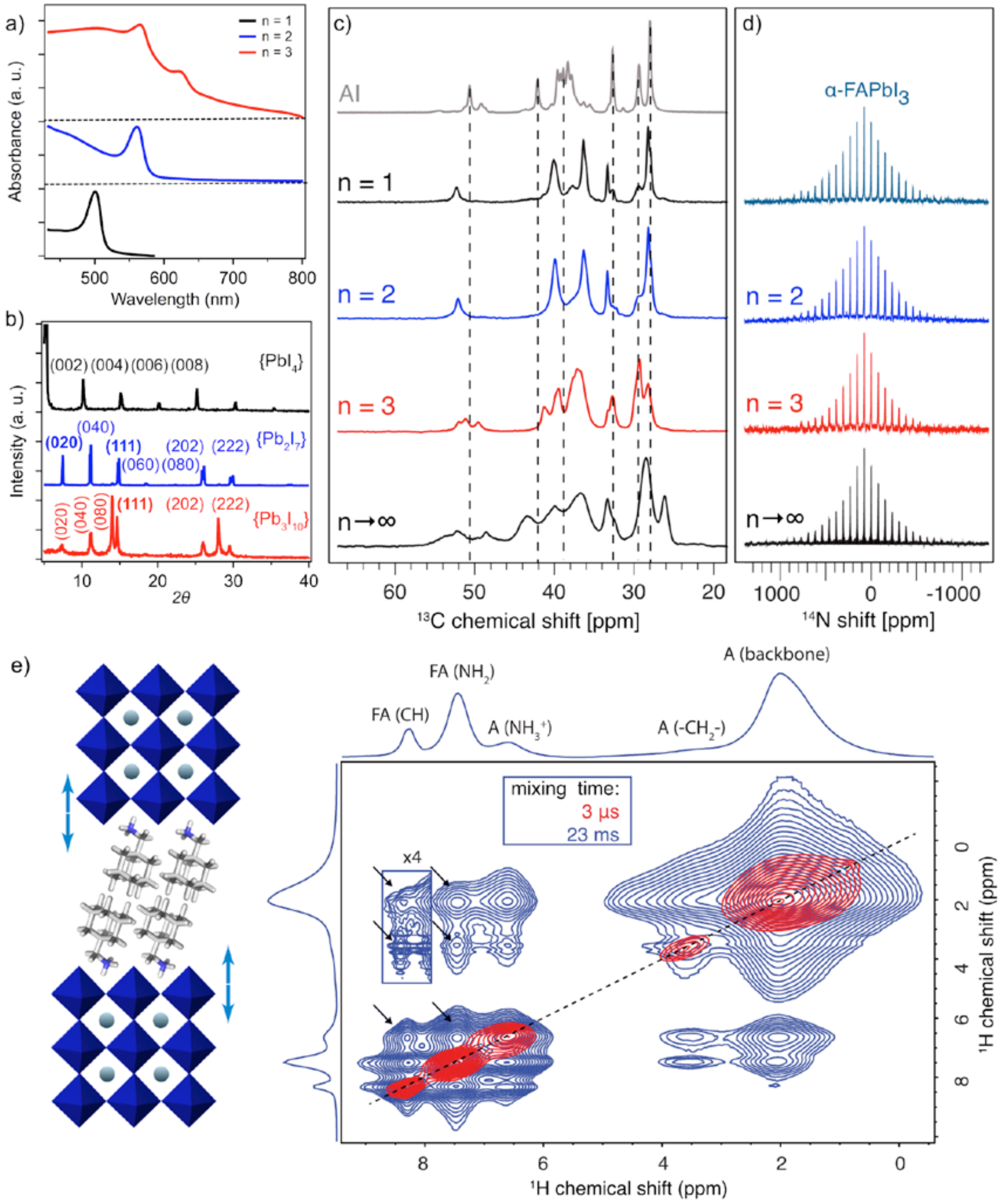

Figure 11. Hybrid layered perovskite Ruddlesden-Popper case. (a) UV-Vis absorption spectra spectra of three different $A_2FA_{n-1}Pb_nI_{3n+1}$ formulations (n = 1, 2, and 3). A = (adamantan-1-yl)methanammonium. (b) XRD patterns on glass substrates for thin films based on the $A_2FA_{n-1}Pb_nI_{3n+1}$ perovskite compositions (n = 1, 2, and 3). The indices of the corresponding planes are based on the Ruddlesden-Popper systems with comparable inorganic phases ($\{PbI_4\}$ for n = 1, $\{Pb_2I_7\}$ for n = 2, and $\{Pb_3I_{10}\}$ for n = 3).[31] (c) ^{13}C CP solid-state MAS NMR spectra at 21.1 T, 100 K, 12 kHz MAS in the spectral area of the spacer (between 20 and 60 ppm) of neat AI and mechanochemical $A_2FA_{n-1}PbnI_{3n+1}$ (n = 1, 2, 3, →∞) powders. The n→∞ system contains a 3D α-$FAPbI_3$ perovskite powder modulated with 3 mol% AI. (d) ^{14}N solid-state MAS NMR spectra at 21.1 T, 298 K, 5 kHz of neat α-$FAPbI_3$ and $A_2FA_{n-1}Pb_nI_{3n+1}$ (n = 2, 3, →∞). CP = cross-polarization; MAS = magic angle spinning. (e) Left: Schematic of the $A_2FA_2Pb_3I_{10}$ composition. The arrows indicate the proximity between the FA cations and the backbone of the spacer, which provides a correlation observed by spin diffusion (SD) experiments. Right: ^1H-^1H SD solid state MAS NMR spectra at 21.1 T, 298 K, 20 kHz MAS of mechanochemical A2FA2Pb3I10 using mixing times of 3 μs (red) and 23 ms (blue). The formulations are defined by the stoichiometry of the precursors and they include mixtures of phases for n > 2 compositions. The region inside a rectangle is magnified to highlight the low intensity cross-peaks. The black arrows show the cross-peaks that evidence atomic-level interaction between FA and A. Adapted from ref.[87] with permission.

from n = 1 (A_2PbI_4) to n = ∞ (α-$FAPbI_3$).[31-35] In addition, as a result of high exciton binding energies, their UV-Vis absorption spectra typically show excitonic features that gradually disappear with an increase in the number of layers.[85] The UV-Vis absorption spectra of $A_2FA_{n-1}Pb_nI_{3n+1}$ (Figure 11a) show strong exciton absorption signals and a gradual red shift of the absorption with an increase in the number of layers (Figure 11a), which is suggestive of the formation of the layered structure. The excitonic absorption peaks are well defined for the n = 1–2 compositions, whereas multiple signals occur for n > 2 compositions, suggesting a mixture of different phases within a single predominant phase (Figure 11a), which is typical for layered hybrid perovskite films. There is evidence that this feature can be beneficial for the electron transfer processes of interest to optoelectronic applications.[85-86]

With analogy to the modulated perovskite systems, the atomic-level microstructure of layered 2D perovskite materials can also be assessed by solid-state NMR spectroscopy. To probe the interaction between the spacers and α-$FAPbI_3$, ^{13}C and ^{15}N MAS NMR spectra at 100 K are particularly insightful.[54-59] The analysis requires comparing the neat spacer, the 2D perovskite compositions (n = 1, 2, and 3), and the 3D phase modified with sub-stoichiometric (e.g. 3 mol%) amount of the spacer ($n \rightarrow \infty$; Figure 11c–d).[51,76] The ^{13}C NMR spectra of the (adamantan-1-yl)methanammonium spacer reveals clear differences between neat iodide salt of the spacer, layered 2D compositions, and the modified α-$FAPbI_3$ phase (Figure 11c).[87] The peaks shift and they are broadened compared to the signals of neat AI, which is in accordance with the existence of the spacer in a new chemical environment, interacting with the $[PbI_6]^{4-}$ slabs, as it would be the case in a layered structure. With the increasing of the n value, the ^{13}C resonances gradually broaden, indicating structural disorder in the FA/AI phases. This is further reflected in the ^{14}N MAS spectra (Figure 11d) of both $A_2FA_{n-1}Pb_nI_{3n+1}$ and modulated α-$FAPbI_3$ ($n \rightarrow \infty$) compositions. Unlike effective modulators shown previously, ^{14}N NMR spectra of layered 2D systems show only subtle narrowing of the SSB manifold compared to the 3D α-$FAPbI_3$ perovskite. In this case, however, for unambiguous evidence of the atomic-level contact between FA and spacer A, it is necessary to demonstrate their presence within the same microstructure at a distance on the order of 10 Å. For this purpose, two-dimensional ^1H-^1H spin diffusion (SD) measurements are particularly relevant (Figure 11e), as in this experiment magnetization exchange is allowed to occur during a longer mixing period, which results in a correlation between species that are within 1 nm distance.[58,87] For instance, the SD spectrum of $A_2FA_2Pb_3I_{10}$ is symmetric around the diagonal, with the diagonal signals corresponding to those shown directly on the two projections (Figure 11e). After a mixing time of 23 ms, a series of off-diagonal peaks appear that evidence the atomic-level proximity between species. This interaction can be either intramolecular (e.g. backbone of spacer) or intermolecular (between the FA cation and the spacer). As the cross-peaks are present in the spectrum for each of the two FA environments (CH and NH_2^+), which is correlated to the chemical environments of the spacer (the backbone, -CH_2^- and -NH_3^+), this unambiguously shows that the two cations exist in the same microscopic phase.[87] The analysis of structural properties of such layered systems is complemented by X-ray diffraction (XRD), as the corresponding XRD patterns commonly reveal the presence of low-dimensional phases through the appearance of low angle reflections in the 2θ range below 10 °. Diffractograms of $A_2FA_{n-1}Pb_nI_{3n+1}$ films on microscopic glass slides show low angle reflections below 10°, typical for layered perovskite materials (Figure 11b).[31-33] While the n = 1 compositions show predominant low angle reflections around 6° associated with (002) reflections that are related to the parallel orientation with respect to the substrate, the n > 1 compositions show a lattice reflection at 2θ °15 that can be ascribed to the (111) plane, indicative of the perpendicular orientation. This orientation is of particular interest to the photovoltaic performance, as it enables effective charge extraction through the inorganic slabs.

The photovoltaic properties of the layered hybrid perovskite solar cells are therefore more effective for the higher compositional representatives (n > 1), which is also in accordance with their optical properties revealed by the UV-Vis absorption spectra (Figure 11a). Moreover, it is apparent that n ≥ 3 compositions feature an onset above 720 nm. This is indicative of the presence of additional 3D phases.[85] Despite the co-existing phases, the highest-performing devices based on $A_2FA_2Pb_3I_{10}$ composition show a short circuit current density (J_{SC}) of 14.3 mA cm^{-2}, open circuit voltage (V_{OC}) of 1.08 V, and fill factor (FF) of 0.50, resulting in a PCE of 7.8% in a reverse scan,[87] which is superior to other FA-based low-dimensional systems.[88] Furthermore, the long-term stability under full sun illumination under inert conditions at ambient temperature show that >84% of the overall PCE is maintained over more than 800 h of continuous operation at their maximum power point. Moreover, storage in humid ambient air with a relative humidity of ~50% maintains >90% of the initial PCE after 900 h. On the contrary, pristine 3D $FAPbI_3$ PSCs lose more than 50% of their performance after <200 h,[88] which emphasizes the potential in the performance and stabilization of layered hybrid perovskite solar cells. In this regard, the most prominent application of layered 2D perovskites is stabilization of highly efficient 3D perovskite materials.

2D/3D perovskite heterostructures are presently the most successful category of hybrid perovskite materials that meet both the performance and the stability requirements. The challenge, however, remains to retain performances comparable to the 3D PSCs with high operational stabilities in ambient air. Further engineering of organic spacer layers provides a productive platform to ascertain this potential, such as by engineering π interactions, through exploiting hydrophobic fluoroarene moieties. There are several examples of fluorine-containing aromatic spacers in layered hybrid perovskites over the past years.[77,89] For instance, a 2D FEA_2PbI_4 perovskite layer employing perfluorophenylethylammonium (FEA) as a fluoroarene cation was inserted between the 3D hybrid perovskite film and the hole-transporting material (Figure 12).[90] As a result of this overlayer, 2D/3D PSCs were shown to retain 90% of their efficiency

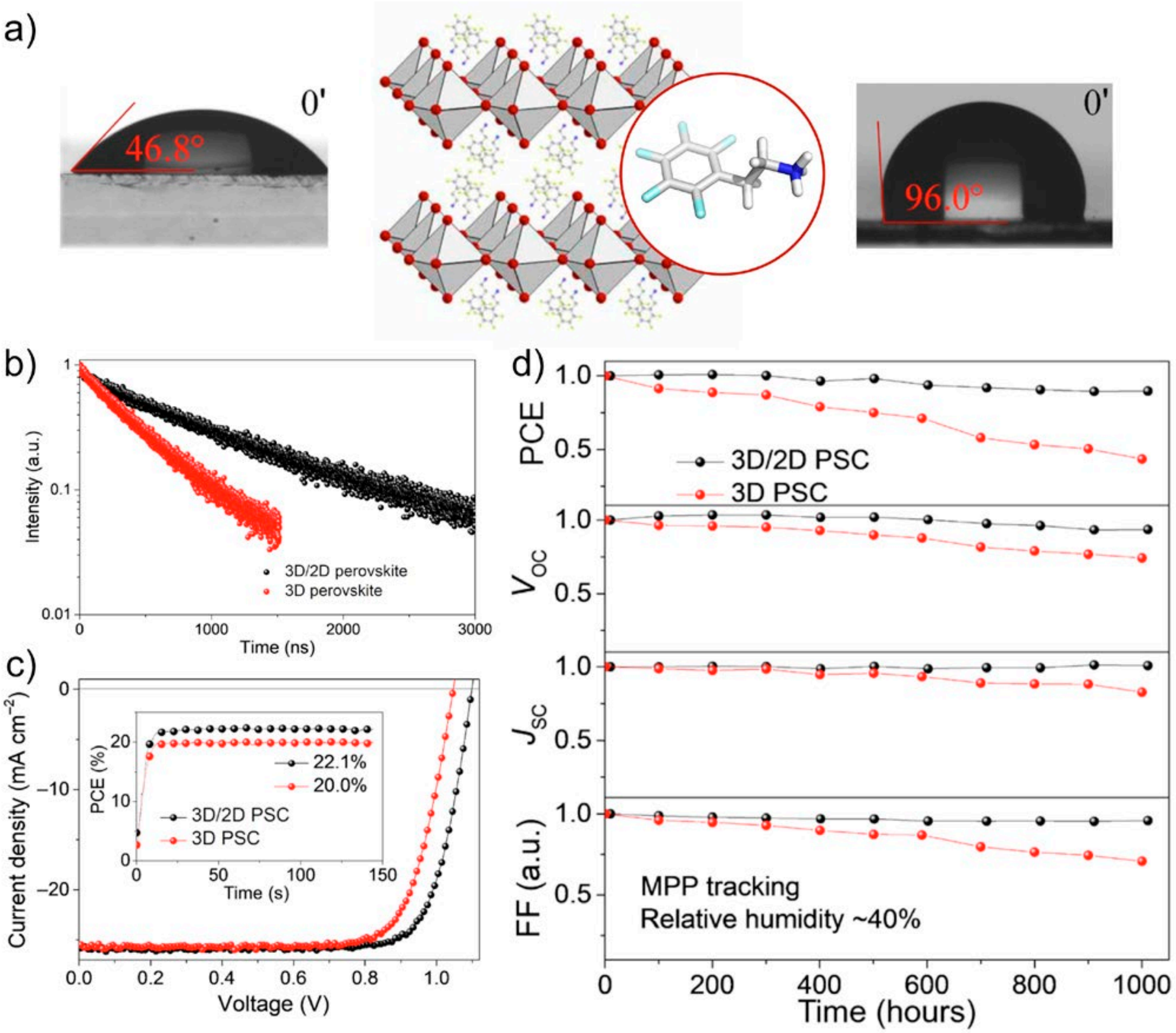

Figure 12. 2D/3D perovskite heterostructure case. (a) Schematic representation of a layered 2D perovskite structure incorporating perfluoroethylammonium (FEA) spacer layer with the contact angle measurements of the neat 3D perovskite (left) and the corresponding 2D/3D heterostructure based on the FEA overlayer (right). (b) Time-resolved photoluminescence decay traces recorded for the 3D and 2D/3D perovskite films. (c) *J-V* curves of a 3D PSC and a 2D/3D PSC with the maximum power point tracking shown in the inset. (d) Ambient atmosphere ageing results of the unsealed 3D and 2D/3D PSCs with the relative humidity shown in the inset. Adapted from ref.[90]

during operation for 1000 h in humid air under simulated sunlight, which is ascribed to high hydrophobicity of the system (Figure 12a,d). Moreover, the 2D layer was also shown to enhance interfacial charge-extraction, suppressing non-radiative carrier recombination (Figure 12b) and resulting in PCE >22% (Figure 12c).[90] These remarkable properties exemplify the beneficial effect of fluoroarene moieties on the structure and morphology of layered perovskite materials, as well as their heterostructures. It can be argued that such systems affect the ionic migration within the active layers of the solar cell through various ion-π interactions, which requires further investigation to exploit these molecular design concepts in the future. Such investigations, in conjunction with solid-state NMR spectroscopic analysis, could set the basis for fully exploiting the strategies of supramolecular chemistry that are effectively employed by natural systems to further advance molecular photovoltaics.

In summary, while a number of challenges with the hybrid perovskites remain to be addressed, recent developments in molecular design and atomic-level investigation open perspectives for further advancements. This is particularly the case in the context of molecular modulation and the development of layered perovskite architectures, which promise to revolutionize the field of hybrid perovskite solar cells.

4. PERSPECTIVES FOR ADVANCING DSSCS AND PSCS

Dye-sensitized and perovskite solar cells have been extensively developed over the past decade, providing sustainable solutions to present energy demands. Dye-sensitized solar cells were inspired by natural photosynthesis and they remain the most powerful technologies for harvesting ambient light to date. Their performances are complemented by an aesthetic appeal, which stimulated the first commercial applications, leading to the current yearly production in the megawatt range. This development involved a number of stages driven by molecular engineering of a variety of dyes and redox shuttles, as well as solvent-free electrolytes based on ionic liquids, fostering industrial applications. Meanwhile, their efficiency remains below the theoretical limit. It is therefore instrumental to focus on the development of solid-state dye-sensitized solar cell technologies. The basis for such systems has already been established over the past years by relying on Cu-based redox shuttles and co-sensitization with organic donor-π-acceptor dye systems. To drive this progress further, unravelling and controlling the interactions in the solid state is essential. Towards this goal, natural systems might be able to provide inspiration. This particularly refers to controlling the assembly of the dyes and redox shuttles by relying on the strategies of supramolecular chemistry, which could enable engineering side-chains of both dyes and redox-shuttles to fine-tune their contacts. This effort should be complemented by the assessment of the potential for utilizing tandem redox shuttles for directing the electron-transfer cascades. Overall, in-depth investigation of the orientation and packing in conjunction with rational supramolecular design can pave the way for overcoming the current performance limitations of dye-sensitized solar cells

On the other hand, as the performance of hybrid perovskite solar cells starts to approach theoretical limits, the research focus shifts towards resolving their stability limitations without compromising the performance. In this regard, two strategies have been particularly promising, namely the molecular modulation and the development of layered two-dimensional perovskite architectures, which was facilitated by the use of solid-state NMR spectroscopy to assess the interactions at the atomic level, setting the stage for advanced molecular design. Further advancements to overcome the challenges can be addressed by relying on the concepts of supramolecular engineering to develop novel supramolecular modulators, as well as layered perovskite materials with superior properties. As structure-property relationships are unravelled at the atomic level, a new platform for rational molecular design emerges to control the underlying processes. Here, fine-tuning the non-covalent interactions can play a major role in controlling the phase purity and orientation of layered hybrid perovskites, while facilitating the implementation of electroactive systems and controlling the ionic motion. In addition, manipulating the interactions between the perovskite and hole- and electron-transporting materials could ensure maximizing the impact of PSCs. These strategies can open the way to combining the functionality exploited in artificial supramolecular systems with solar energy conversion. We predict that this approach will play a major role in the near future, as more innovative strategies emerge to control the properties of light-harvesting materials and the corresponding solar cells.

ACKNOWLEDGEMENT

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Singlet Fission: Toward More Efficient Solar Cells

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Abstract. A survey is provided of the current status of singlet fission as a tool for bypassing the Shockley-Queisser limit on the efficiency of single-junction solar cells.

Keywords. Solar cells, Shockley-Queisser limit, singlet fission, photophysics, solid state packing.

INTRODUCTION

The human mind is remarkable in many ways. One of them is its ability to disregard reality in order to induce pleasant feelings. I know for sure that my wife of 50 years, who recently unexpectedly passed away, will never return. Yet, several times a day, I catch myself expecting her to open the door and smile at me. Twice a year, I tell my students that there will be a final examination at the end of the semester. They ignore this repugnant thought blissfully, since the distant future is of no concern. A few days before the exam, when disaster is at the door, they start coming and asking what they are expected to know. I doubt that as a student I was any better. No wonder that much of the general public and numerous influential politicians deny that the incipient climate change has anything to do with human activities, least of all with the burning of fossil fuels, although in sober moments they must surely realize that thousands of climate scientists actually know their business. After all, the most serious consequences of climate change are not yet at the door, unlike many immediate and apparently more important issues of the day that are.

I suspect that the tendency to deny inconvenient reality and cherish immediate gain at the expense of distant troubles are in our genes and must have offered evolutionary advantages in some distant past. They surely do not offer long-term advantages now and our generation will be cursed by all that follow. Past generations did not know what effects a drastic rapid increase in the concentration of carbon dioxide in the atmosphere will have. We do and yet on the whole we act as if it did not matter.

Given the nature of the human mind, it seems to me that the best gift that science and engineering could presently offer to mankind is to make sustainable energy economically preferable. This is not an easy task. However, if solar, wind, and other forms of energy generation that do not contribute to climate change were cheaper than the burning of fossil fuels, hardly anybody would burn fossil fuels and the already inevitable damage would be limited.

SOLAR CELLS AND THE SHOCKLEY-QUEISSER LIMIT

The largest potentially available source of safe renewable energy is solar radiation, and an increase of the efficiency or reduction of the cost of solar cells would go a long way toward reducing the currently huge release of greenhouse effect gases. Many scientists and engineers are working on this task all over the world and great strides have been made in recent decades. In many parts of the world, the goal appears to be realistic, although well recognized and very formidable technical obstacles stand in the way, such as the need for large-scale energy storage and for transportation fuels.

Unfortunately, the energy efficiency of inexpensive solar cells is limited to about 1/3 (the Shockley-Queisser limit[1]). These cells contain only a single junction (interface) at which negative and positive charges separate to proceed to their respective electrodes, The primary cause of the limitation is the broadband nature of solar radiation, whose photon energies range from the infrared to the ultraviolet. No matter how small or large we choose the bandgap of a solar cell material, which determines the maximum voltage produced, there always are some solar photons with less energy than the bandgap that are not absorbed and utilized, and others that have more energy than the bandgap. The latter are absorbed but their excess energy is almost immediately converted into vibrational energy and ultimately wasted as heat.

The current produced by a solar cell is limited by the number of photons absorbed and the voltage is limited by the size of the bandgap. A smaller bandgap permits the collection of a bigger fraction of the incident photons and hence leads to a larger current at the cost of generating a smaller voltage. A larger bandgap will produce a higher voltage but will cause a smaller fraction of the photons to be absorbed and therefore will generate a smaller current. The power generated is the product of the current and the voltage, and the best compromise is to choose a bandgap of about 1.1 electronvolt (eV), which provides a theoretical efficiency of about 1/3 (Figure 1), a limit that has been approached but not quite reached by modern silicon cells. Little further improvement of the efficiency of single junction cells is possible.

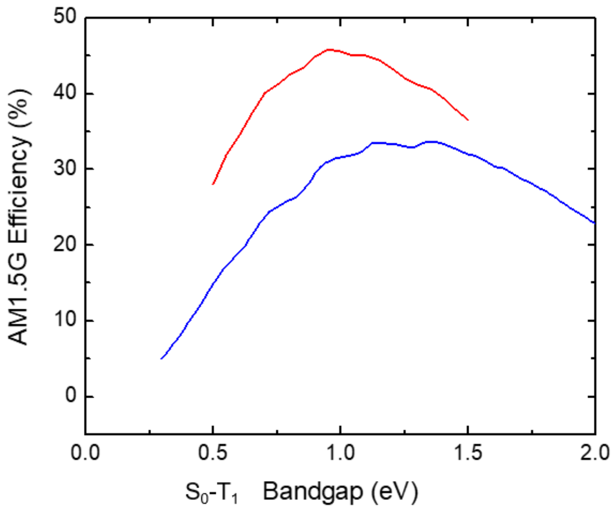

Figure 1. Maximum theoretical efficiency of a single-junction solar cell, assuming 1 sun illumination, full absorption of incident solar light above 1.1 eV, detailed balance, 200% triplet yield in the singlet fission layer, and production of an electron-hole pair from each triplet. Bottom curve (blue): ordinary; top curve (red): top layer, singlet fission and bottom layer, ordinary. Reproduced by permission from Hanna and Nozik.[2]

All this has been known for over half a century, ever since Shockley and Queisser, his postdoc at the time, published their pivotal paper.[1] Once I asked Prof. Queisser about the correct pronunciation of his name (it is German, kwi-ser) and he told me about the hard time they had when they tried to get the article accepted for publication. The reviewers did not see anything wrong in the derivations, but they felt that the results were of no theoretical or practical interest and publishing them would waste precious journal pages. Half a century later, this may well be one of the most quoted paper ever published in the journal. I mention this story to remind myself and others not to get discouraged when our papers are not immediately accepted for publication and proposals for funding.

BEYOND THE SHOCKLEY-QUEISSER LIMIT

Overcoming the Shockley-Queisser limit at low cost is a stimulating challenge. True, the use of cells containing multiple junctions with different bandgaps already has led to efficiencies approaching 1/2. However, since the currents flowing through each junction need to be matched, the fabrication is very demanding and so expensive that such cells are suitable only for special uses, for instance on space vehicles. They are valuable, but using them does not have much chance to be cheaper than burning coal.

Several other schemes have been proposed for going beyond the Shockley-Queisser limit, promise to be inexpensive, and are the subject of intense research. One of them is multiple exciton generation (MEG), which relies on solids in which each high-energy electronic excitation can be converted into two or more lower energy electronic excitations faster than it is converted into vibrational excitation and thus ultimately into heat. Then, each absorbed low-energy photon is used to produce a single electron-hole pair as in ordinary solar cells, while absorbed high-energy photons act as if they were two or more low-energy photons. As a result, a smaller fraction of their high energy is converted into heat and efficiency rises.

Materials known to behave in this manner are of two types: (i) semiconductor nanoparticles and (ii) organic molecular solids. The most obvious difference between the photophysics in the two is the absence of a clear distinction between singlet an triplet excitations in semiconductors and its presence in organic molecular solids. The latter are the subject of the present article.

The conversion of a singlet exciton into two triplet excitons, known as singlet fission (Figure 2),[3,4,5,6] was first observed over half a century ago.[7] Since the two triplets are coupled into an overall singlet when they are first born, the process is spin-allowed. It can be very fast and can outcompete all other decay modes, providing an up to 200% triplet yield. The fundamental nature of the phenomenon was elucidated in half a dozen years after the initial discovery and thereafter interest in it died off. It revived early in this century when Hanna and Nozik pointed out that a combination of a top layer of singlet fission capable material followed by a bottom layer of an ordinary solar cell material would increase the maximum theoretical efficiency of a solar cell to almost 1/2 (Figure 1).[2] No current matching would be required and the cost would remain low. A similar suggestion in this direction was made even earlier by Dexter but did not elicit much attention until very recently. By now, singlet fission has been shown in two laboratories to provide an external quantum efficiency over 100%.[9,10,11,12,13]

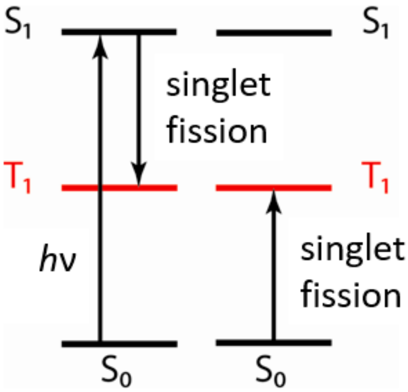

Figure 2. Schematic representation of singlet fission.

SINGLET FISSION SOLAR CELLS

Why, then, if the theory is understood and the principle proven in the laboratory, are singlet fission solar panels not commercially available after a decade of intense effort in many laboratories? The problem has to do with finding a practical singlet fission material and with moving charges out of it into a useful electrical circuit. A truly practical material must produce two triplets upon absorption of nearly every photon of sufficient energy. This will occur if singlet fission outcompetes all other modes of excited state decay, which is only possible when the process is exothermic or only slightly endothermic. It should not be too exothermic, since that would incur a loss of efficiency by converting electronic excitation energy into vibrational and subsequently into heat. For the maximum efficiency to approach 1/2, the singlet excitation energy should be about 2.2 eV and the triplet excitation energy, about 1.1 eV. The two triplets must separate easily, must be long-lived, and must move readily through the material in order to reach an interface where the negative and positive charges are to separate. During their travel to this junction, the triplets should not encounter any of the separated charges, because these quench triplet excitation efficiently to generate the ground state and heat.[3]

There is another reason for insisting that singlet fission must occur very fast, even if there are no competing decay processes other than the relatively slow fluorescence, which occurs on a nanosecond time scale. Ordinarily, singlet excitation moves through a molecular solid much faster than triplet excitation. Although singlet excitation is much shorter lived, nanoseconds instead of microseconds, it still may reach the interface where excitation separates into charges before singlet fission has had a chance to occur, especially if the initial excitation occurred very close to or right at the interface. If this happens, only one electron-hole pair will result and efficiency suffers.

The requirement of approximate thermoneutrality of the singlet fission process imposes a demanding condition on the energies of the lowest excited singlet and triplet levels in the solid, $\Delta E(S_1)$ and $\Delta E(T_1)$, respectively:

$$\Delta E(S_1) \geq 2\ \Delta E(T_1) \qquad (1)$$

Only a handful of compounds, mostly tetracene, pentacene, and their derivatives, are known to meet the condition and to perform singlet fission with full efficiency. Unfortunately, structures of this type are notorious for their inability to withstand the combination of light and air. Yet, a practical singlet fission material must continue to function after a long time of exposure to sunlight under ambient conditions. It is possible to protect it from the atmosphere with a suitable coating, but the more perfect the insulation against traces of oxygen, the higher the cost.

In addition to meeting the conditions imposed by the requirements of singlet fission, the material must meet many others that are common to all solar cell materials: for instance, it should have a high absorption coefficient for all visible and ultraviolet photons with energies above the absorption threshold, and its redox properties must be appropriate for the intended separation of charges at the junction.

Assuming that all these potential pitfalls are avoided, all the necessary conditions met, and the charges generated at the junction are successfully brought to electrodes, the question remains, how do we identify an optimal practically useful singlet fission material? The search can be subdivided into two tasks: (i) What molecular structure do we choose? (ii) How do we pack the molecules in the solid? Before addressing these issues, the singlet fission mechanism needs to be described in more detail.

SINGLET FISSION MECHANISM

The process is rather complex and provides many opportunities for decay to the ground state, all of which need to be bypassed if triplet yield is to be 200%. In Figure 3, the desirable path is indicated by narrow blue arrows and the decay paths by stubby red arrows. The introductory event is the absorption of a photon, which generates a singlet exciton. This contains a single excitation, which is however typically shared among half a dozen or perhaps a dozen adjacent molecules in the solid. Note that in contrast, a triplet exciton would be usually localized on a single molecule.

Singlet fission consists of two main events. First, the singlet exciton is converted into a singlet biexciton, a molecular pair in which each partner is in its triplet state and the two triplets are coupled into an overall singlet. Second, the spin state of the biexciton transforms from singlet to a mixture with quintet and triplet, and the two triplet excitations separate as two free and independent triplet excitons whose spins usually remain coherent ("entangled") for tens of nanoseconds. We shall consider the two main events separately.

(i) Formation of a biexciton

The singlet exciton may meet one of several fates. It can undergo singlet fission to produce two triplet excitations as desired, but it can also undergo intersystem crossing to produce a single triplet, it can form an excimer, it can form a charge-transfer state, in which one molecule has transferred an electron to a neighbor, and it can perform a photochemical reaction. If all of these processes are too slow, it will ultimately fluoresce. The formation of a biexciton typically occurs without any intermediates and its rate can be approximately divided into a dominant "superexchange" contribution mediated by virtual singlet charge-transfer configurations and a usually negligible "direct" contribution provided by the two-electron part of the interaction Hamiltonian.

In rare cases, the relative energy of the charge-transfer configurations is so low that they describe real states that correspond to minima in the potential energy surface of the first excited singlet S_1. They then have a finite lifetime and are actually observable. They still have an opportunity to generate a triplet biexciton and sometimes they do,[14] but mostly they take one of two other undesirable options. One is internal conversion to the singlet ground state by back electron transfer, with a complete loss of all the excitation energy as heat. The other option is intersystem crossing to the nearly isoenergetic triplet charge-transfer state. In that instance only half of the original excitation energy is lost, and one triplet exciton is generated. It may be difficult to tell whether the origin of observed triplets is singlet fission or this type of intersystem crossing.[15]

In certain solids limited molecular motion is relatively facile.The crystal structure may permit two of the molecules that share the initial singlet excitation to approach each other and form a stabilized stacked pair, known as an excimer. Its wave function typically contains comparable amounts of the initial locally excited configurations and charge-transfer configurations, whose energy has been lowered by the approach of the two partners. The excimer is often considerably stabilized relative to the original exciton and its conversion to a biexciton is usually too endothermic to compete with radiative and non-radiative decay to the ground state.

It is likely that the formation of charge-transfer states, which also can compete with singlet fission from the singlet exciton, is merely a more extreme version of the process of excimer formation. If the approach of the two molecules stabilizes the charge-transfer configurations so much that they dominate in the excimer wave function, even a small dissymmetry that favors electron transfer from one partner to the other over electron transfer in the opposite direction will collapse the wave function in the more favorable direction and form a radical ion pair, known in solution as an exciplex, and in the solid as a charge-transfer state. The facility of the collapse is due to the very small value of the interaction element between the two charge-transfer configurations, which only contains contributions from the two-electron part of the Hamiltonian. Once again, the exciplex is usually stabilized too much relative to the original exciton to permit its conversion to a biexciton. As noted above, such states usually decay to the singlet ground state by back electron transfer, or to a triplet exciton by intersystem crossing to the nearly isoenergetic triplet charge-transfer state.

(ii) Formation of free triplet excitons

Once the singlet biexciton is formed, the path to its dissociation into two independent triplet excitons

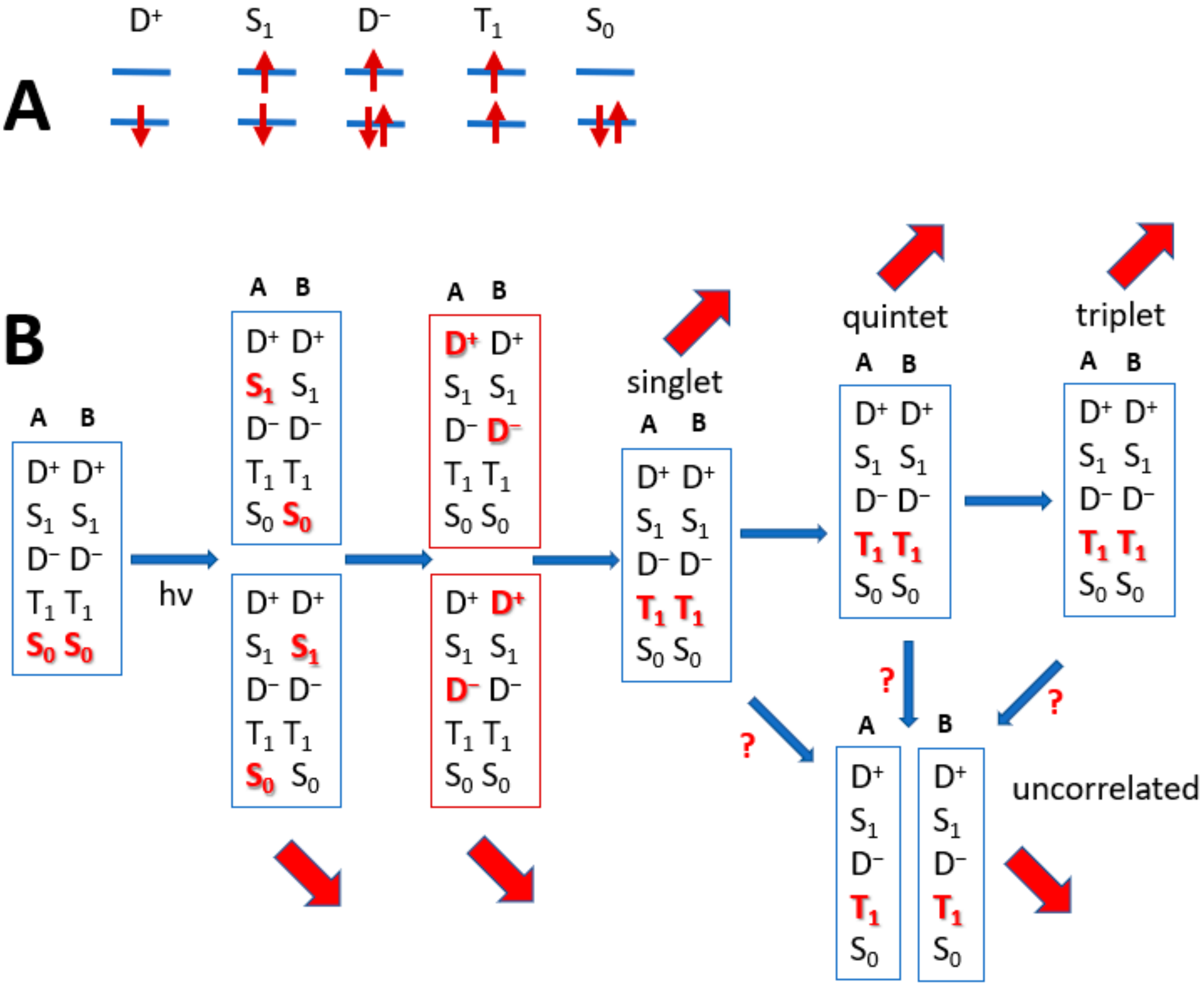

Figure 3. A: Symbolic representation of states available to molecules A and B. B: The general mechanism of singlet fission. The possible electronic configurations of partners A and B are listed in black and the actually occupied configuration is shown in red. Frames located above each other indicate the sets of configurations that need to be mixed to form a state. Black frames indicate real states and red frames show states that usually are only virtual. Thin blue arrows indicate the path for singlet fission and fat red arrows indicate undesirable decay channels. See text.

may appear to be smooth. In reality it is anything but smooth, and the yield of free triplet excitons is often disappointingly low. Although the calculated biexciton binding energies are usually quite small and the dissociation should be fast, the decay of the biexciton to two ground state molecules, or possibly to one ground state and one triplet molecule, tends to compete successfully. Unfortunately, relatively little is known about the mechanisms involved.

First of all, we need to note that the conversion of a singlet exciton into a singlet biexciton is reversible.[16] The reverse process is known as triplet-triplet annihilation. An exact reversal yields the singlet exciton back and delayed fluorescence may be observed. Two free triplet excitons can still be formed, but it will take longer and this is not helpful. Conversion of the singlet biexciton into the singlet ground state of both molecules might be expected to be slow because of the large energy gap, but often it is fast and competitive with the desired dissociation into two free triplet excitons. The mechanism that makes it so is not understood, and conceivably the process goes through the intermediacy of the quintet or triplet states of the biexciton. If it goes solely through the singlet manifold, it might possibly be related to events that occur during photochemical pericyclic reactions, specifically photocycloadditions.[17,18] In these reactions, the ground state of the starting material correlates with a doubly excited state of the product and vice versa. This correlation produces a conical intersection ("pericyclic funnel") half-way along the reaction path, through which the excited molecule or molecular pair returns to the ground state surface and then partitions between starting material and photocycloadduct. Since the doubly excited state has a singlet biexciton (double triplet) character, it is conceivable that the decay of the biexciton formed in the first step of singlet fission involves an approach toward the same conical intersection. The lowest energy point of the intersection would not have to be reached before decay to the ground state potential energy surface becomes rapid. At this point, however, this is pure speculation.

If the biexciton has time to modify its spin function, the reverse process might produce a triplet excited molecular state. Formation of the lowest triplet state would be strongly exoergic and probably quite slow, but if the excitation energy of one of the next higher molecular triplet states lies only a little below the energy of the biexciton, it might be formed fast. Subsequent internal conversion would afford the lowest triplet and this decay process would then represent the conversion of the singlet biexciton to one triplet exciton, a significant loss. Although such a process has apparently not yet been observed with certainty, in order to minimize its likelihood it is desirable although probably not essential to complement the condition expressed in equation (1) with the condition $\Delta E_{T2} > 2\ \Delta E_T$.

In principle, the biexciton might also convert to a molecular quintet excited state, but this will hardly ever be energetically possible. After all, even the lowest molecular quintet state is a doubly excited state and the condition $\Delta E_Q > 2\ \Delta E_T$ is fulfilled more or less automatically.

Why should the wave function of the singlet biexciton change its spin part into triplet or quintet so easily when it is an eigenfunction of the electrostatic Hamiltonian and only some very minor additional terms in the full Hamiltonian can be responsible? The relatively facile intersystem crossing is enabled by the nearly exact degeneracy of the singlet, triplet, and quintet states of the biexciton. Then, even the very weak magnetic dipole - magnetic dipole interactions, familiar from electron paramagnetic resonance spectroscopy of triplets (zero-field or D, E tensor), are able to induce intersystem crossing. The levels can also be mixed by Zeeman terms due to an external magnetic field and indeed, the sensitivity of singlet fission to external magnetic fields was one of its early recognized hallmarks.[19]

According to theory, the initial conversion should be from the singlet biexciton to the quintet biexciton, which has already been observed,[20,21]and then to triplet.[3,19] These pathways, and the paths from the three spin states of the biexciton to free excitons and to the ground state, are currently under intense scrutiny. The separation into two independent triplet excitons that are spatially separated seems to occur by a hop of excitation in one of the triplet partners in the biexciton to a neighboring ground-state molecule, similar to the hopping motion of triplet excitons through the solid.[22]

MOLECULAR STRUCTURE

Some of the structural requirements on the molecules to be used in singlet fission materials are dictated by common knowledge. The need for high absorption coefficients and absorption onset near 2.2 eV is generally satisfied by the use of extended π-electron systems. The redox properties can normally be controlled by a choice of substituents. The need for slow intersystem crossing is usually met by avoiding heavy atoms and low-lying $n\pi^*$ states. Suppression of fast internal conversion calls for structural rigidity and absence of structural elements with low-frequency vibrations. Inspiration for light fastness is provided by industrial dyes.

The condition that is the most difficult to meet is the location of the lowest triplet level (T_1) approximately half-way between the ground (S_0) and first excited (S_1) singlet levels.[23] In most ordinary molecules, T_1 and S_1 result from the same promotion from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and are separated by approximately twice the exchange integral between these two orbitals. This integral is very small for $n\pi^*$ excitations and excitations with strong charge-transfer character, in which the HOMO and the LUMO avoid each other in space. It is also small in most non-alternant hydrocarbons and in contrast, tends to be large for alternant hydrocarbons (no odd-membered cycles). Thus, large alternant hydrocarbons tend to be good choices. Tetracene and pentacene were recognized as suitable a long time ago, and a derivative of a large alternant hydrocarbon, terrylene, has also been recently shown to perform well.[23] A more general group of compounds that was recognized early on as providing suitable candidates are biradicaloids, compounds that are part way between perfect biradicals and ordinary molecules. In the former, the S_0-T_1 gap is typically much smaller than half the S_0-S_1 gap, and in the latter, much bigger. In between, there is a range of biradicaloid structures where the two are comparable. Considerations of this type led to a set of guidelines for the choice of two partially overlapping sets of chromophores that meet the energy criterion, large alternant hydrocarbons and biradicaloids.[22] Theoretical requirements for the use of biradicaloids have subsequently been elaborated[24,25,26,27] and several biradicaloid structures have been identified as suitable candidates computationally.[22,27,28,29,30] So far, only one of these proposals has been tested. The compound in question is 1,3-diphenylisobenzofuran, which was indeed found to be highly efficient.[31] However, the triplet yield was up to 200% in only one of its two very similar known crystal modifications, and was a mere ~15% in the other.[32]

PACKING IN THE SOLID PHASE

The above observation leads us to the second variable in singlet fission materials, and that is the packing of the selected molecule in the solid phase. There is ample evidence that it plays a critical role in determining the suitability of a compound as singlet fission material.[34] We leave aside the difficult question of methods for enforcing a particular packing, whether by crystal engineering or synthesis of non-conjugated covalent dimers, and focus on the need to know what packing to aim for. This was not clear in the past, but recently theory has provided some advice. This is available in the form of a publicly available computer program Simple,[34] which finds the local maxima of the rate constant for the formation of a singlet biexciton from a singlet exciton by singlet fission as a function of all physically possible geometrical arrangements of a pair of rigid π-electron chromophores (six degrees of freedom). Geometries in which the molecules interpenetrate are excluded. The output consists of the best geometries, drawn in the order of decreasing relative rate constant, and an example[35] is provided in Figure 4.

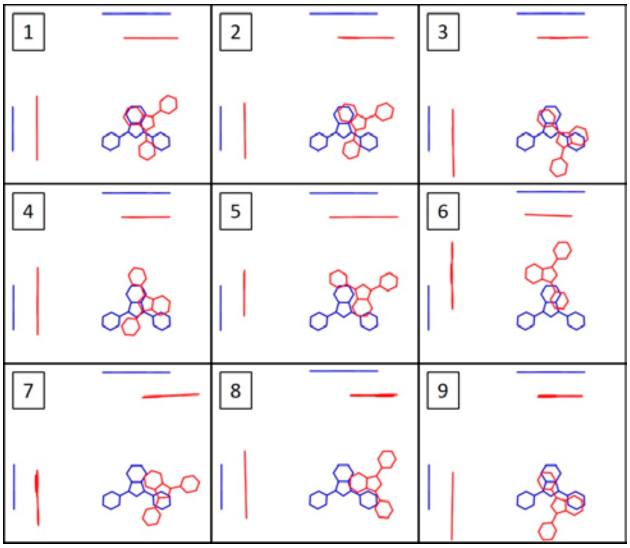

Figure 4. Multi-view projections of the nine best pairs of the C_2 rotamer of 1,3-diphenylisobenzofuran optimized for the rate of singlet fission. The computed rate constants for biexciton formation relative to the rate computed for the structure actually found in the crystal, in the order 1-9, are 4306, 2944, 2261, 896, 892, 806, 717, 546, and 536.

The calculation is based on the Fermi golden rule, according to which the rate is proportional to the square of the electronic matrix element for singlet exciton into biexciton conversion and the density of states at the energy of the biexciton. It involves the evaluation of the electronic matrix element at billions of geometries but is still quite fast, because it uses a series of physically motivated and tested[34,36] approximations. The relative rate constants are evaluated using Marcus theory, and the program has been used without problems for molecules as large as cibalackrot, with 36 atoms in the conjugated π-electron system of each member of the pair.[36]

A simplified version of the theory was used to develop pictorial rules for evaluating the suitability of a pair geometry, which require only the knowledge of the approximate shapes of the frontier orbitals of the molecule, HOMO and LUMO.[37,38]

Inspection of the results for several chromophore choices suggests that two dominant factors determine the relative rate of singlet fission at the optimized geometries. They are, first, the size of the squared electronic matrix element, and second, the energy balance of the process. The former enters directly into the Fermi golden rule and the latter, along with the reorganization energy, enters the Marcus equation. The energy balance is not determined solely by molecular properties. It depends strongly on the size of the Davydov splitting, the separation of the two levels into which an exciton pair is split by intermolecular interactions. After vibrational equilibration, the exciton level that is energetically lower will carry the bulk of the initial population. If it is stabilized excessively, it will not have enough energy to produce a biexciton, even if in the isolated molecule the T_1 level was positioned ideally half-way between the S_0 and S_1 levels. Instead, the exciton will decay to the ground state, radiatively or radiationlessly.

The magnitude of the Davydov splitting can be approximated as four times the electrostatic interaction between the S_0-S_1 transition charge densities on the two molecules, which in turn can be roughly estimated from the interaction of their transition dipoles. It vanishes when the dipoles are perpendicular to each other and this goes a long way toward an explanation of the twists seen in the optimal pair structures shown in Figure 4. These geometries reflect a compromise between the tendency of the electronic matrix element to favor strong overlap of the two molecules and the proclivity of the dipole-dipole interaction to minimize their interaction and vanish at orthogonally twisted geometries.

INTRAMOLECULAR SINGLET FISSION

This survey would not be complete if we did not mention singlet fission in which the two generated triplet excitons reside in different parts of the same molecule, known as intramolecular singlet fission. When the interaction between the two covalently connected chromophores is strong, especially when the bridging unit or units are capable of π conjugation, it becomes difficult and ultimately even impossible to distinguish the now intramolecular singlet biexciton state from other intramolecular singlet excited states and the use of the term singlet fission could then be questioned. It would be unusual to refer to the internal conversion of the optically allowed B_u state of 1,3-butadiene into its “double triplet” A_g state as singlet fission, although their wave functions suggest it. It is not obvious just where to draw the line.

A case of particular interest are conjugated polymers, but only a few recent references can be provided here.[39,40,41,42,43] In such polymers, the two triplet excitations can move quite far apart on the same chain, and also jump to separate chains. It is then certainly appropriate to talk about singlet fission. As long as the two excitons stay on the same chain and only undergo a one-dimensional diffusion, they have a high probability of re-encountering each other, and it is then important that they do not mutually annihilate. As discussed above, such a reverse of singlet fission would often provide ample opportunities for ultimate decay to the ground state with a release of heat.

SUMMARY

In conclusion, it is fair to say that singlet fission is now known to be a much more complicated process than it appeared to be before the recent spurt of activity in the field, and that there are many ways in which it can go astray. It is possible that a practical material for singlet-fission solar cells will be recognized tomorrow, but it is also possible that it will take many years. I believe that the ultimate goal, making sustainable energy less expensive than the burning of fossil fuels, is important enough to make it worth turning over every stone on the beach.

It should also be recognized that by their very nature, scientific discoveries build on each other in unpredictable ways. The fundamental understanding of the photophysics of organic molecular systems that is generated in the studies of singlet fission may end up being the largest gain from the enterprise, and may turn out to be valuable in very unexpected contexts. For example, perhaps the initial spin coherence (“entanglement”) of the two triplet excitons generated by singlet fission might be utilized in quantum information science? After all, when Bunsen and Kirchhof discovered that the sodium D line is a doublet, their discovery must have appeared to have no practical consequences. They could not have foreseen that they have launched a process that will lead to the concepts of electron spin, nuclear spin, magnetic resonance spectroscopy, and a century and a half later, imaging of brain tumors!

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A Green New Deal: The Economic Benefits of Energy Transition

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Abstract. After explaining the current climate emergency, this survey article summarises financial cost estimates for transition to zero carbon by 2050, which even in the medium term, neglecting catastrophic climate collapse, are much less than the cost of 'business as usual' (BAU). Standard economic modelling of continued GDP growth with only minor costs of climate change and limited mitigation investment which still guides policy is shown to be completely unrealistic, simply ignoring current climate science, health costs and the welfare economics of economic growth. The global health benefits from phasing out fossil fuels will also exceed the costs of transition to renewable energy in the medium term, and these co-benefits are widely neglected. The major investment and fiscal expansion required for rapid transition will help to attain full employment, further reducing the net financial cost of the policies necessary for energy transition to avoid catastrophic climate change, policies often summarised as a 'Green New Deal'.

Keywords. Climate catastrophe, energy transition, renewable energy, fossil fuel, pollution.

1. INTRODUCTION

Atmospheric CO_2 concentrations have been rising steadily, with a 2- 3 ppm increase p.a., reaching a record 415 ppm in May 2019 (the highest for about 3 million years), although estimated carbon emissions from fossil fuels (FF) remained roughly constant for 3 years, mainly due to the substitution of cleaner gas for coal,[1] before increasing again in 2017. Emissions of greenhouse gases from land use change and biomass burning are more difficult to estimate and probably account for the steady growth of atmospheric CO_2.

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[1] UK emissions in 2017 were 42% below 1990 levels due mainly to replacing coal by gas, according to official accounts, but neglecting the outsourcing of 'dirty' production to China and other developing countries, as well aviation and shipping. Including these factors means that consumption-related emissions have declined by only about 10%, as pointed out by climate activist Greta Thunberg (Carbon Brief, 2019; Anderson, 2019). China remains the world's largest emitter and user of coal by a wide margin, as well as being the largest investor in RE, and though coal production seems to have peaked, there is no sign yet of the rapid reduction needed to reduce even appalling local pollution with health costs from 9 – 13 % of GDP , let alone mitigate climate change (LSE, 2018).

The really bad news is that the Arctic is warming twice as fast as the temperate zones, under the influence of positive feedbacks – albedo effects as ice and snow cover recede, and growing methane emissions from rapidly thawing permafrost – thus threatening eventually irreversible, runaway warming without drastic and rapid mitigating action. Otherwise the result could be a largely uninhabitable, 'hothouse earth' with much higher temperatures than previously predicted, or experienced for millions of years, and resulting collapse of current civilization (Steffen et al, 2018; Berners-Lee, 2019; McKibben, 2019; Wallace-Wells, 2019). *'The only rational response to the scientific evidence on climate change, is to declare a global emergency – to mobilise all of society to do whatever it takes to fix it'* (Paul Gilding, 2018).

Mean global temperature is already more than 1 degree C above the pre-industrial level, and *'... paleoclimatology has revealed that in the longer run each 1°C of warming will result in 10 to 20 metres of sea-level rise and that the current level of greenhouse gases is sufficient to produce warming that would likely end human civilisation as we know it...'* (Spratt, 2019)

Yet the latest, 2018 report by the Intergovernmental Panel on Climate Change, *Global Warming of 1.5°C: An IPCC Special Report*, warns of serious consequences from exceeding 1.5°C, but neglects the major threats already posed by current warming, not to mention further warming triggered by Arctic methane release and other positive feedback effects. Loss of Arctic and Antarctic ice has been accelerating in recent years, and only a rapid drawdown of existing atmospheric CO_2 has a chance of averting major, long term sea level rise. Lack of policy recommendations follows the conservative tradition of official UN reports, which have all failed to call for the required emergency, WWII-scale mobilisation of investment to phase out FF as rapidly as technically possible (Spratt, 2019).

Since the cost of energy transition varies considerably between nations, and there are also incentives for national governments to 'free-ride' or rely on mitigation by others, strong international agreements for cost sharing and meaningful sanctions are essential to accelerate the process. Such agreements would have to go far beyond the ineffective United Nations Framework Convention on Climate Change (UNFCCC) Paris Agreement, or the badly designed EU emissions Trading System, neither of which have had much success in facilitating energy transition. Ironically, Swedish schoolgirl Greta Thunberg's Fridays for Future, school strike campaign and other movements such as Extinction Rebellion, have done much more to focus public opinion on the climate emergency in many countries, with a widespread upsurge in Green Party votes and a first commitment by new EU Commission President Ursula von der Leyen to attain carbon neutrality by 2050.

To avoid widespread collapse of water supplies and agriculture in populous regions, which is most likely to be the first major climate related disaster if emergency policies are not rapidly implemented, other measures are also needed. Reducing food waste, deforestation and meat consumption, and transition from industrial factory farming to sustainable eco-agriculture, are all urgently required for food security, which includes halting the parallel emergency of accelerating biodiversity loss (SDG, 2019).[2]

The 1.5°C target is arbitrary, and evolving temperatures cannot be predicted at all precisely from actual emissions paths and policy measures. The target is likely to be exceeded, at least temporarily, even if all emissions were suddenly stopped, due to the thermal inertia of the large ocean mass, which takes a long time to reach equilibrium temperature with relatively slow circulation from the surface down to the depths. Eliminating aerosol air pollution from biomass and FF burning, which has a substantial cooling effect, would actually accelerate warming in the short run, and require further drawdown of atmospheric CO_2. Much faster warming of the critical Arctic region also reduces the relevance of mean global temperatures.

A CO_2 concentration of 350 ppm is considered to be the maximum 'safe' level and is thus a much more relevant target (though the pre-industrial level was only 280 ppm), since the current warming trend began at about this level in the 1970s. Nearly half of current emissions are sequestered by natural sinks. However, ending deforestation, and additional carbon sequestration through reforestation and a switch from industrial monocultures, which promote soil carbon loss, to regenerative eco-agriculture and agro-forestry will be needed, in addition to rapid transition from FF to RE, to reduce the atmospheric carbon concentration to 350 ppm by 2050. Industrial hemp can sequester 10 tonnes of carbon per hectare per year, in poor soil with little water and no need for fertilizers, so is much more effective than slow growing tree plantation. (Hawken, 2018; Rumpel et al, 2018). These policies have already been shown to be highly cost-effective at local levels, and are much more promising than carbon capture and storage (CCS), which has proved to be very costly and ineffective in several discontinued tri-

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[2] Whether political response will be rapid enough to avert disaster remains an open question, with plenty of grounds for pessimistic scepticism in spite of a surge of 'green votes' in the 2019 European Parliament elections, but with strong right wing populist support forclimate science denial as well.

als in the US (Grandia, 2018). Sgouridis et al (2019) show in detail that RE investment is much more cost-effective that any likely development of CCS, though of course technological breakthroughs cannot be ruled out.

It is ironic that the dangers of climate change had already been clearly identified by 1989, when pioneering scientist James Hansen testified before the US Congress, and the first IPCC had been constituted, with little progress over the intervening 30 years, or indeed at the latest, December 2018 COP24 conference at Katowice (Revkin, 2018). New research by Yu et al (2018) provides strong evidence that 1.5°C of average warming will be reached by about 2030 on present trends or 'business as usual' (BAU), 10 years earlier than predicted by the 2018 IPCC *Special Report*. One estimated global carbon budget of cumulative emissions for not exceeding 1.5°C will exhausted by 2020 under BAU, underlining the urgency of radical mitigation and 'drawdown' policies for which only the political will is lacking (Hawken, 2018; Hickel, 2017).

The good news is that solar and wind power costs have been declining much faster than only recently predicted, to reach or fall below parity with FF generation costs in favourable locations, but this development is rather overwhelmed by the still limited share of wind and solar (WS) in global primary energy consumption (only about 1.5%, though estimates vary), and totally inadequate investment. Nuclear remains the most expensive new power source, but closing down existing nuclear power for purely party-political reasons, while only planning to phase out heavily subsidised coal by 2038, as in Germany's expensive but ineffective 'Energiewende', will remain one of Chancellor Angela Merkel's worst legacies (*Der Spiegel,* 2019).

Estimated WS capacity is just over 1 trillion watts (TW), currently growing at about 17% p.a. with investment under $300 billion pa (and recently declining in monetary terms). Jacobson et al (2017) estimate about 50 TW of new wind, water and solar (WWS) capacity would be needed by mid-century for a zero carbon economy, which would thus require an average expansion of about 1.6 TW p.a. over the next 30 years to attain, more than 10 times the current annual WS[3] addition! Of course, this could only be achievable with initially still higher growth rates, underlining the catastrophic inadequacy of current 'business as usual' climate and energy policy (BAU), which will generate only a slow decline of the FF primary energy share of about 80%, as well as a rapid overrun of the 'safe' global carbon budget, and a probable 'hothouse earth'. Sgouridis et al (2016) investigated the dynamics of a complete transition to renewable energy including storage from a net energy perspective while staying within the carbon budget. To achieve this, installation rates would peak at around 8TW p.a. in 2035, and emissions could be cut by more than half by 2030 with major energy savings and parallel 'drawdown' of atmospheric carbon through eco-agriculture and industrial hemp plantation.

Jacobson et al (2017, 2018, 2019) analyse several technically feasible models of decarbonisation. One estimate gives a total gross investment cost for transition by 2050, at about $125 trillion or an average annual cost of just over $4 trillion,[4] which, as we argue below, represents a less demanding policy shift for the rich countries that will have to bear most of the cost than the WWII mobilisation which finally ended the Great Depression in the US (McKibben, 2015; Tooze, 2019). This estimate is quite conservative, neglecting likely major further improvements in WS or any other, new RE technologies, but does assume large scale efficiency gains and savings through electrification. These numbers are of course only a rough guide to gross costs, and neglect the extensive co-benefits of transition discussed below. Hawken (2018) provides detailed discussion of many different technologies to 'drawdown' carbon and transition to RE, with similar overall conclusions. A comprehensive new report by Ram et al (2019) estimates a much lower cost of global transition to 100% RE by 2050.

Behavioural changes such as much higher cycle and public transport shares in urban areas, less flying, meat consumption, deforestation and material use in an economy based on repair and recycling rather than obsolescence and disposal, will also be necessary to ensure rapid enough transition and avoid shortages of crucial materials.

In the next section 2, we offer a brief account of traditional neglect and fundamental misunderstanding of the climate emergency by prominent economists. In section 3 we then summarise the evidence that mobilising society for energy transition would yield enormous medium term financial, health and employment 'co-benefits' that would more than pay for transition, in addition to averting catastrophic climate change as the ultimate long term '*bonus*'. Section 4 explains the macroeconomic and distributional benefits of the 'Green New Deal' (GND) or mobilisation for energy transition, all the more urgent after decades of neoliberal austerity. A detailed discussion of the main policies for a GND follows in section 5, while section 6 relates these policies to the 'growth or de-growth' debate. Conclusions are summarised in a final section 7.

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[3] Most of the new capacity would be WS, since there is only limited scope for expanding (mainly small scale) hydro power.

[4] Presumably in constant, current dollars, roughly 5% of current global GDP.

2. TRADITIONAL ECONOMICS OF CLIMATE CHANGE AND ENERGY TRANSITION

Long after the threats of unmitigated climate change, pollution and environmental destruction had been recognised by environmentalists and scientists, these issues were ignored by most economists. The 2018 Nobel laureate economist, William Nordhaus, was an exception who did make early attempts to quantify the 'optimal' carbon tax with the help of long-term models of GDP growth and possible climate damage known as 'integrated assessment models' (IAMs), but nevertheless assumed growth to be much more important than climate damage and essentially unlimited.[5] Future damages are reduced to trivial present values using unreasonably high discount rates, and future generations are assumed to be so much richer that they can easily cope with climate change! His latest attempt (Nordhaus, 2017), estimates the welfare maximising 'social cost of carbon' or optimal tax rate at $31 per ton, rising by about 3% p.a., which would only slightly reduce the BAU emissions path. He predicts 'mean warming of 3.1°C for an equilibrium CO_2 doubling' by 2100, without considering the methane and other feedbacks which would almost certainly generate much higher temperatures and a largely uninhabitable 'hothouse earth' under such a policy. With average annual real per capita growth predicted to be about 2%, mainly due to exogenous technological change, climate damage is claimed to be only about 2% of GDP by 2100, though much of the world's population might not survive this BAU programme!

All these model predictions are decisively contradicted by the climate science which is never mentioned by Nordhaus. It is now clear, as Steffen et al (2018) and others have shown, that even the old 'political' target of 2°C average warming, let alone 3.1°C, would decimate global food production, and trigger irreversible methane and other feedbacks to leave much of the world uninhabitable in the long run, with warming ultimately far beyond 3.1°C. *'What is more, Nordhaus reasons that the sectors most vulnerable to global warming—agricultural, forestry, and fishing—contribute relatively little to global GDP, only about 4 percent. So even if the entire global agricultural system were to collapse in the future, the costs, in terms of world GDP, would be minimal'* (Hickel, 2018). On this logic, billions of the world's poorest inhabitants contribute relatively little to Global GDP, so their death from starvation would also hardly matter. Furthermore, water and products of the vulnerable sectors are universally under-priced, neglecting externalities and sustainability, and encouraging overuse and exploitation.

In addition to the moral repugnance of these conclusions, they are also based on elementary economic errors. If agriculture was devastated by climate change, most of the rest of the global economy would collapse, and food prices would explode, so while billions of the poorest inhabitants would starve, what was left of the agricultural sector would actually *dominate* global GDP because inflated spending on food would exhaust most budgets even in rich countries! This is likely to be the first really major global impact of climate change, long before rising sea levels have flooded many of the world's biggest cities, because modern industrial agriculture in general and many of the most important food growing areas in China, India, and Africa, as well as the wheat belt of the North American Great Plains are particularly vulnerable to increasing aridity, falling water tables, rising temperature and extreme weather events as climate change progresses.

A major reduction of meat consumption and food waste could feed the current population with a much smaller total output, as well as greatly reducing FF use and emissions, and providing healthier diets, but in addition, large - scale conversion to regenerative eco-agriculture, and ending deforestation are necessary for long term sustainability. This incorporates mixed farming, low-till cover-cropping and controlled animal grazing, to reverse accelerating soil carbon loss, degradation and desertification under current destructive and unhealthy industrial agriculture, with its reliance on intensive factory farming and large-scale, vulnerable monocultures, to sequester a substantial share of carbon emissions (Holt-Jimenez, 2019; Hawken, 2018; Rumpel et al, 2018; FitzRoy and Papyrakis, 2016; Montgomery, 2016).

While Nordhaus's ideas seem to have provided academic respectability for policy makers' obsession with growth and neglect of food security and climate mitigation measures, other prominent economists,[6] never cited by Nordhaus (2017), have clearly recognised the possibility of catastrophic climate change and the impossibility of any meaningful cost-benefit analysis of, for example, the destruction of much of human and other terres-

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[5] Bardi (2018, 2011) discusses Nordhaus's repeated failure to understand 'complex systems' of ecology and economy, as modelled in the Club of Rome's Limits to Growth and various updates (Meadows and Randers, 2004).

[6] See Stern (2015), and Wagner and Weitzman (2016). These studies as well as the latest climate and environmental science and the threat to global food production are all ignored by Nordhaus (2017), although they clearly show that all his central assumptions are completely unrealistic. However these and most other economists have neglected the co-benefits of transition discussed below.

trial life, so that policy priority should just be the fastest politically 'feasible' transition to zero carbon. Such a policy will minimise the expected cost of ongoing climate change as well as the risk of more distant disastrous outcomes. In this respect, these economists follow the lead of climate scientists, but like Nordhaus, neglect the much earlier, pioneering work of ecological economists such as Daly (1973, 1992) and environmentalists such as McKibben (1989), who have long recognised that drastic reduction of emissions with a mobilisation of resources almost comparable to that of WWII (but lasting for decades), represents the only safe and viable climate policy, which would also provide many co-benefits. Indeed, full employment after the Great Depression was only restored by war time mobilisation in the US.

As Gilding (2018) remarks, '*The only rational response …is to do whatever it takes*', which must again mean the fastest 'feasible' transition, where the constraint is how rapidly behavioural changes such as less driving, flying and meat-eating can be implemented in the wider population with help of 'nudges' and persuasion in a democratic framework. What is not widely realised, due to the well-funded efforts of the FF lobby to exaggerate the costs of transition to RE, as well as denying the costs of climate change, is just how small – actually *negative* – the real overall *net* costs of transition are likely to be, though of course the FF sector will be the main loser with all their 'stranded assets' left in the ground.[7]

3. THE COST-REDUCING AND HEALTH-IMPROVING CO-BENEFITS OF ENERGY TRANSITION

In addition to the obvious benefit of saving the natural world and human civilization from irreversible and catastrophic climate change in the long run, transition to RE offers three additional major co-benefits in the medium term (Hawken, 2018; FitzRoy and Papyrakis, 2016; Smith, 2013). The most obvious is perhaps the reduction of expenditure on FFs as they are replaced by RE, thus reducing the net cost of transition. The IEA (2019) estimates world FF energy investment of about $1.5 trillion in 2018, about 2% of global GDP, so the average annual total direct cost of BAU could be nearly half of the average annual $4 trillion cost of complete transition in the next 30 years, following Jacobson et al (2017). They also estimate that nearly 13% of total end-use energy world-wide is used to *produce* the refined FF and uranium that provide most of the current energy supply. All FF costs are likely to rise substantially as the most easily exploited resources are declining and reliance on unconventional, 'tight' oil and gas and costly fracking increases. Total FF cost savings will depend on the precise path of RE expansion, but should be substantial, at least in the later stages, though rapidly expanding RE and efficiency investment will initially raise FF demand which is a necessary component of what was termed the Sower's Way – the use of FF for building the RE infrastructure (Bardi, et al, 2016).

The second co-benefit or cost saving has recently been highlighted by the IMF, where Coady et al (2017) estimate the current global costs of air pollution from FF, including about 4 million annual fatalities from outdoor air pollution, at around $4 trillion in 2015, roughly equal to the projected average cost of transition! However Burnet et al (2018) and Lelieveld et al (2019) find 9 million – twice as many – fatalities p.a. from ambient (outdoor) fine particulate, or $PM_{2.5}$, and ozone pollution, with much improved data and estimates, greater than the 7 million annual deaths from smoking found by the WHO. Indoor air pollution from cooking with solid fuels and traditional stoves are a major additional source of mortality and morbidity in developing countries, but with less quantitative data. All this obviously implies much higher costs, at least double the IMF estimate, depending on how the morbidity and mortality of poor individuals is evaluated. Over 90% of the fatalities are in poor countries, which is why the imputed value of a statistical life (VSL) of about $1 million, or less with morbidity costs included, is only a small fraction of the VSL in advanced economies. Thus following the new studies, $10 trillion or about 13% of global annual GDP would seem to be a very conservative, rough estimate of annual health and well-being costs from FF pollution.[8]

These costs have two components – the direct, financial or resource costs of lost output, disability and extra costs of care and medical services, and the intan-

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[7] See McGlade and Ekins, 2014; Rogeli et al, 2015. An alternative is compensation or a public sector buyout of FF assets in order to reduce opposition with a Pareto improvement for all (Broome, 2018; Smith, 2019), not an appealing policy after decades of deception and disinformation, a campaign which was clearly contradicted by ExxonMobil's own early research results. Smith (2019) emphasises that displaced FF-affected workers do need to be given alternative employment and training.

[8] Most of the fatalities are among vulnerable individuals with a much lower life expectancy than the average, but this is often the result of a long history of exposure. Pollution also directly reduces happiness of all who are affected, as well as the future health, life expectancy and IQ of children who suffer exposure. Huge health costs from indoor air pollution due to biomass burning for cooking in developing countries should be added, and could also be largely eliminated with cheap solar energy and clean cookers, adding substantially to the benefits from transition to renewable energy. Scovronick et al (2019) estimate that 'The global health benefits from climate policy could reach trillions of dollars annually…'.

gible, welfare costs of premature mortality and morbidity, as well as directly reduced life satisfaction for most people affected. These latter costs are usually estimated as the VSL, and the value of QALYS – quality adjusted life years – by willingness to pay for a marginal reduction in the probability of fatality or morbidity, or for a cleaner environment, which in turn implies dependence on income and hence large differences between rich and poor countries, an ethically dubious distinction. We do not have separate estimates of the intangible and tangible components, but even just the latter are likely to exceed the approximately $4 trillion estimated average annual cost of complete transition to a zero carbon economy by 2050.

Coady et al. (2017) refer to the total imputed cost as 'post-tax subsidies', which are much greater than direct or pre-tax financial FF subsidies of less than $1 trillion p.a. Economists usually refer to external costs of pollution rather than subsidies, but not accounting for these costs with an appropriate 'Pigouvian' tax on FF does amount to an implicit subsidy which has substantially increased FF consumption and consequent environmental and health damage.

Pollution costs have been steadily increasing under BAU, and some health damage from pollution will continue to emerge after the pollution is reduced or eliminated. Nevertheless, avoiding a growing share of at least $(2+10 = 12) trillion direct and indirect or external annual costs of FF as RE grows and replaces FF suggests a very approximate average annual saving of half the total, or $6 trillion.[9] This is much larger than the Jacobson et al (2017) estimate of annual average cost of transition, leaving a huge co-benefit in addition to averting irreversible and catastrophic climate change as the ultimate 'bonus'. Of course, health and other costs of pollution would increase rapidly under continued BAU, well beyond 2050, until the industrial global economy collapsed under the impact of climate change, and most of the global population died, so these 'estimates' are very conservative, rough guides to orders of magnitude. Furthermore, the health benefits from a zero carbon economy would continue *indefinitely* after 2050, so even in terms of discounted present values, the surplus of cost savings or benefits over the actual expected costs of transition to RE would be still further increased, a huge reward over and above the essentially incalculable benefit from averting catastrophic climate change.[10]

4. GREEN NEW DEAL

Various co-benefits of 'steady state economics' and energy transition have long been emphasized by environmentalists such as McKibben (2016, 2006, 1989) and progressive economists, such as Daly (1973, 1977), and recently by the Green New Deal Group and New Economics Foundation in their 'Green New Deal' proposal (NEF, 2008; Murphy and Hines, 2019).[11] After the financial crash of 2007/8, 'quantitative easing' (QE) – the purchase of government bonds by central banks – helped to fuel an asset price boom, making mainly the rich even richer and contributing to growing inequality, with little effect on employment. Austerity then inflicted huge losses on the majority, as most wages have stagnated and welfare spending cut, particularly in the UK and US, while un- and particularly under-employment remain serious problems everywhere (Storm, 2017; Blanchflower, 2019).

The Keynesian alternative would have been a major fiscal expansion to fund labour-intensive investment in infrastructure and energy transition in a Green New Deal, creating jobs for genuine full employment, and a start to averting irreversible climate change. ECB expenditure of €2.4 trillion on QE, ending in 2018, was a gigantic missed opportunity, as were similar QE programmes in the UK and US (Tooze, 2019).

The Keynesian 'multiplier' effect results as increasing employment reduces the need for welfare and unemployment benefit payments, so the formerly unemployed will start to pay taxes, while their greater spending will in turn stimulate the rest of the economy and further raise tax receipts. Thus some of the original extra public expenditure will be recouped, further reducing the net cost of RE and other public investment before the economy reaches full employment, with little danger of increasing inflation in the current environment of very low interest rates and inflation. Prospects of 'secular stagnation' advanced by prominent economists strengthen the case for further fiscal stimulus (Eggertsson et al, 2018; Tily, 2017).

Launching a programme of rapidly expanding RE and related investment will require initially increasing

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[9] Summarises for simplicity a linear increase of savings from initially 0% to finally 100% of projected total FF costs of at least $14 trillion p.a. As noted above, some of the health costs and hence savings are intangible.

[10] Hawken (2018) summarises of savings from complete decarbonisation by 2050 of $74 trillion with a very different methodology, but without distinguishing between pecuniary and non-pecuniary components, and using the outdated Coady et al (2017) health cost estimates, which could explain why the total is somewhat lower than the estimates reported here. It is not clear whether the total represents final accumulated savings or a present discounted value. However the similar orders of magnitude from such disparate approaches are quite reassuring.

[11] The idea is receiving increasing attention from progressive Democrats such as Alexandria Ocasio-Cortez, the UK Labour Party and Green Party supporters in the US and Europe, though neoliberal media disinformation and neglect have so far hindered any broader public understanding or acceptance (Roberts, 2018; Klein, 2019; Rifkin, 2019).

public expenditure and funding requirements before the multiplier effect begins to generate rising revenue and reduce welfare claims. While the dysfunctional Euro system raises serious legal obstacles to such necessary policies (Mody, 2018), there are no real problems for countries with sovereign currencies such as the UK, where central banks can simply create necessary funds without causing inflation, as long there are underutilised resources, and governments can borrow or raise taxes on high earners. As Tooze (2019) puts it, '*A decade after the world bailed out finance, it's time for finance to bail out the world*'.

However, conservatives obsessed with the neoliberal ideology of smaller government, lower taxes for the rich, less welfare for the 'undeserving' poor, and 'debt fetishism', have imposed austerity in the UK and much of the EU since 2010 at enormous cost in both human and economic terms. They continue to oppose fiscal expansion, neglect infrastructure and underfund the NHS and care services, while completely failing to understand the urgency of climate change mitigation (Cooper and Whyte, 2017). And more broadly, the ad hoc Maastricht criteria for Eurozone members place all emphasis on debt and budget deficits, ignoring employment, poverty or any environmental/CC targets. The official UK Climate Change Committee (CCC, 2019) has published detailed plans for zero carbon by 2050, now also an officially legislated target, but there are currently no signs of needed policies.

Conservatives in the US including most of the Republicans in Congress and the Trump administration generally deny basic climate science[12] (as well as modern economics and even evolution), as do Vladimir Putin in Russia and Brazil's new President Jair Bolsonaro, so the political prospects for rapid implementation of serious climate policy even in Europe, let alone in other major polluters, are still extremely dim. China leads in RE investment but also in emissions and coal consumption by a wide margin, and while coal use may have peaked, appalling pollution problems remain, and the urgently needed, rapid reduction of coal powered generation has not yet been addressed, while China continues to support new coal power in many developing countries.

5. POLICIES FOR ENERGY TRANSITION

The co-benefits outlined above are all medium to long term, and so major additional initial expenditure remains necessary. Economists agree that substantial and rising carbon taxes should be part of any climate policy, but to gain public acceptance and avoid adverse distributional effects, at least some of the revenue should be returned, either as an equal per capita 'dividend' to all citizens as part of a universal basic income, or targeted to the most disadvantaged. While redistributive in aggregate because the rich generally use more FF- carbon per head than the poor,[13] there are always some low income households with a high FF consumption, e.g.in rural areas, who would need additional compensation (Boyce, 2018; Stiglitz and Stern, 2017). Subsidised electric cars for low income individuals with long commutes and lacking access to public transport would have obvious benefits to mitigate the distributional impact of a carbon tax, as would the expansion of low cost or free public transport (as recently introduced in Luxembourg). Banning most cars from cities would greatly facilitate cycling, socialising and public transport with major health and welfare benefits, and be much more effective than current plans just to replace petrol and diesel cars with still very expensive e-cars, or indeed with *any* motorised individual transport.

Extensive and sometimes violent, 'Gilet Jaunes' protests erupted in France in late 2018 in opposition to rising fuel taxes, initially announced without any compensation or redistribution of revenues, thus illustrating the importance of distributional equity, and finally forcing the Macron government into cancelling the fuel tax hike and several neoliberal policies which also reduced the incomes of low earners. As Mehling (2018) explains, subsidies for RE are also needed to accelerate development and gain broad acceptance, and higher taxes which impact low income households need to include appropriate compensation, in contrast to purely redistributive taxes on high earners, which should then be used to benefit the poorer majority of the population. Under such appropriate conditions there is actually widespread support for a global carbon tax (Carattini et al, 2019). Unfortunately some commentators such as Martin Wolf in the Financial Times (5 Nov, 2019) claim without evidence that large scale public investment in mitigation implies abandoning markets in favour of a 'planned economy' with disastrous effects. He fails to understand that it is far too late to rely exclusively on carbon taxation.

To alleviate the inevitable disruptions of transition to RE, as well as problems already being caused by the growth of non-standard and precarious employment

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[12] Even those who claim to accept the evidence for climate change generally still deny the need for urgent policy measures to reduce FF use.

[13] In the US, the top 10% of the income distribution emit over 4 times as much carbon per head as the bottom 10%, and globally they are responsible for about half of total emissions. However Boyce (2018) shows that a \$200 / t CO_2 US fee-and-dividend would leave 12% of the lowest income quintile, and 23% of the 2nd quintile worse off, so the need for additional compensation is clear, some of which could come from a universal basic income.

for many, a modest universal basic income for all citizens, combined with a public sector job offer or guarantee, seems to be the most effective policy to supplement existing and unco-ordinated, targeted welfare measures (FitzRoy and Jin, 2018)

A carbon tax or 'fee-and-dividend' which is not too high to be disruptive initially, but rises on a pre-announced path to ultimately capture the full external costs of FF use, and thus undo the existing implicit subsidies discussed above, should provide the appropriate incentives for the private sector to invest in energy saving and RE. However direct government and central bank intervention, 'green bonds' and subsidies will surely be required for rapid change on the required scale, less than WWII mobilization when military spending peaked at 41% of GDP, but lasting for decades (Tooze, 2019). In particular because the very fast growth of RE capacity needed to achieve largely complete decarbonisation by mid-century will impose initially rising costs, supply-side bottlenecks and shortages. Certainly to build the continental -scale smart grids and storage and back-up facilities needed to 'smooth' the natural intermittency of local RE production will require major public investment and international political coordination in Europe and elsewhere. Smith (2019) and others argue in detail that only 'eco-socialism' with public ownership of large corporations can manage rapid transition, though it is difficult to see why appropriate regulation and other policies cannot achieve the same goal.

Contrary to frequent claims, higher taxes are not necessary initially, though reducing growing inequality with more progressive, redistributive taxes on high incomes would have many political and welfare benefits, but obviously faces strong opposition. Instead, as long as there are underutilised resources in the economy, sovereign governments and their central banks can create new money, or borrow without risk of generating inflation or default, to fund the vital and productive investment of a Green New Deal. As the additional expenditure is re-spent by the initial recipients and thus raises other incomes, this Keynesian multiplier mechanism will increase government tax revenues and over time can offset much of the initial investment cost.

The first stages of a massive expansion of RE will also require additional FF energy, which may even require a temporary increase of FF production if energy saving elsewhere does not proceed fast enough. Sgouridis et al (2016) have estimated that FF supplies should be adequate for transition with the growth of unconventional or 'tight' oil and gas, in spite of the decline in easily recoverable reserves and the 'energy return on energy invested' (EROEI).

The intermittency of WS is frequently claimed to be a major obstacle to complete decarbonisation. However Jacobson et al (2017, 2018), Breyer et al (2018), Brown et al (2018) and Ram et al (2017) have shown in detail that an appropriate combination of continental-scale smart grids, feasible storage technologies and closed cycle gas turbine back- up generating capacity, using bio-gas or even natural gas, can smooth supply and solve the intermittency problem at a cost which is dwarfed by the value of the energy savings from almost complete electrification. Since the back-up will only be required during very rare, extreme weather conditions persisting over large areas, the average annual emissions from use of natural gas during such events will be negligible. In Europe, for example, the sunny Mediterranean periphery would be optimal for solar, and could be linked to the windy north for night time wind power generation by a high voltage, direct current, 'smart grid' with very low transmission losses, and additional savings potential when coupled with smart metering and household appliances.

An important but neglected point is that moving from 'low' to zero emissions is the most expensive phase of transition. Particularly since existing natural sinks would be substantially augmented by adoption of eco-agriculture and large scale reforestation, a small, remaining share of flexible natural gas for power generation, as a back- up to variable renewables, could greatly reduce storage and other costs and still allow a steady reduction in the stock of atmospheric CO_2 concentration to the target of 350 ppm. Complete decarbonisation may thus be an unnecessarily ambitious and expensive goal, though the final trade-offs will need careful calculation and monitoring. The main priority must be the initially rapid reduction of emissions through energy saving and expansion of RE while phasing out coal consumption, and cutting globaal emissions by at least half by 2030.

6. GREEN GROWTH, DE-GROWTH OR BOTH?

There is a long standing debate about the feasibility of continuing (greener) GDP growth on the transition path to a zero carbon economy and subsequently, or whether radical reduction of currently wasteful and polluting production and consumption will be required, and if so, how the costs of such de-growth should be distributed (Antal and van den Bergh, 2017; Jackson, 2018; Semieniuk et al, 2018; Schröder and Storm, 2018). There does seem to be general agreement, at least among environmental economists, that complete decoupling of GDP growth from environmental damage is an illusion (Ward et al, 2016). However, this debate sometimes diverts attention away from the crucial supply-and-demand synergy of expanding RE, replacing first coal, and then other FF power as rapidly as possible, and simultaneously reducing energy demand by investment in energy efficiency and saving. Thus there is extensive scope to retrofit buildings for greater energy efficiency, and replacing ICE vehicles with EVs, including public transport, and bicycles.[14] Much of this activity is labour intensive, and under a Green New Deal full employment should be attainable, with rising incomes for the formerly un-and-underemployed, and increasing public expenditure, so that GDP would certainly grow in the initial stage of transition. However this growth would be mainly in investment, though with some consumption growth for the newly employed and low income households who benefit from redistributive carbon fee-and-dividend payments and a universal basic income, as well as more progressive taxes on the rich.

Clearly developing countries need green growth to attain the Sustainable Development Goals, but equally obviously, the developed economies cannot continue material growth indefinitely, with ever more and ever larger cars and houses which use many other scarce resources in addition to energy. Indeed, radical conservation and savings policies will be needed, including repair and maintenance of durable goods instead of the 'throwaway culture' of planned obsolescence. In the long run the 'levelized cost of electricity' (LCOE),[15] after transition to RE is estimated to be lower than the BAU LCOE largely powered by FFs in the many studies referenced above, but it will not be zero (though the *marginal* cost of RE up to capacity limits is very low with no FF use). Thus there will continue to be limits to the recycling of non-renewable resources, and hence to sustainable material (and population) growth. On the other hand, declining IT costs facilitate the 'weightless' growth of human knowledge, though the resulting power of digital 'natural monopolies', the proliferation of 'fake news', and the potential for intrusive surveillance, abuse and addiction in digital social networks remain serious threats, still far from being effectively regulated (Zuboff, 2019).

Though ignored by policy makers and academic GDP growth proponents such as Nordhaus (2017) and Friedman (2006), but emphasised by Nobel Laureate economist Joseph Stiglitz (2009; 2019), Kubiszewski et al (2013) and many others, it has long been known that GDP is a poor measure of welfare, and that *'[c]hasing GDP growth results in lower living standards. Better indicators are needed to capture well-being and sustainability.'* (Stiglitz, 2009). Since the pioneering work of Easterlin (1974, 2013), a large and expanding body of survey evidence shows that subjective well- being, life satisfaction or happiness are unrelated to economic growth in the long run in developed economies, though short-term fluctuations are positively correlated. This is mainly because unemployment and loss of income are major causes of unhappiness, and also because *relative* income is an important determinant of happiness above the poverty level, which does not change when all incomes are growing simultaneously (Kaiser and Vendrik, 2018).

Though income is correlated with well-being in cross sections at any time, the effect is weak for income above the poverty level. The main determinants of happiness are satisfying work, health and family and social relationships, as well as environmental quality. Even worse, growing inequality in recent decades has eroded both well-being for the majority who have not benefitted from economic growth, and the basic institutions of democracy (Atkinson, 2015; Dorling, 2017; Stiglitz, 2013; Wilkinson and Pickett, 2010, 2018). In the UK, only the minority with higher education and earnings reported increasing life satisfaction over the last two decades, while in the US average happiness has declined since the 1970s, with greatest decline for the poor (FitzRoy and Nolan, 2018; Graham, 2017).

In an egalitarian society with minimal poverty and deprivation, technological progress can be used to reduce working time and improve work-life balance following practice in Social Democratic Denmark and other Nordic economies, which also regularly yield the highest life satisfaction or happiness rankings (Gustavson, 2011; Radcliff, 2013; Lakey, 2016). In addition to transition to RE, another, complementary, transition, from neoliberal obsession with GDP growth to priority for well-being and sustainability is urgently required (Laurent, 2017). As Jackson (2016) and many others have emphasised, 'prosperity without (material) growth' is then the only sustainable, long run alternative in advanced economies to currently prevailing 'growth fetishism' and environmental destruction, though of course knowledge should continue to grow, and poor countries still need to overcome poverty with aid for green growth.

7. CONCLUSIONS

Concern about climate change is increasing in populations around the world as the effects become

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[14] Such policies have already dramatically improved the quality of urban air and life in cities such as Copenhagen, Freiburg, and, remarkably, in Curitiba, Brazil (FitzRoy and Papyrakis, 2016).

[15] The net present value of the unit-cost of electricity over the lifetime of a generating asset, including both investment cost and operating cost, equal to the break-even average price. Aghahosseini et al (2019) find that complete transition of power generation to RE in the Americas by 2030 would already reduce the LCOE compared to BAU

increasingly evident. However, the perception that complete transition to RE would be inordinately expensive remains widespread, a perception which is not only the result of intensive FF lobbying and disinformation efforts. Proponents of RE remain preoccupied with the undoubtedly spectacular technical progress and falling costs of RE, but have generally failed to make the economic case that rapid global energy transition under the necessary massive mobilisation with a Green New Deal would provide a financial and welfare bonanza.

Much of the world's advanced economies remain mired in 'secular stagnation' a decade after the Great Recession, with high levels of underemployment and declining labour force participation, not captured in official unemployment statistics. At the start of WWII, the US was suffering from even worse problems from the legacy of the Great Depression in the early 1930s, with over 14% unemployment, which was reduced to about 1% by 1944, while GDP doubled with military spending that peaked at 41% of GDP. A Green New Deal of similar magnitude today could also generate truly full employment to save the environment and reverse 'global heating', with immense and *immediate* benefits for the most deprived, un-and-under-employed who are currently suffering from neoliberal policies and shrinking welfare. It is these and other short to medium term co-benefits of energy transition and climate change mitigation which are most likely attract widespread political support from electorates whose immediate survival concerns tend to crowd out warnings of apparently distant climate catastrophe.

Thanks in particular to the pioneering work of Stanford's Mark Jacobson and his co-authors we now know that average annual costs of energy transition by 2050 are of similar magnitude to the financial savings from phasing out FF and averting just the local health costs of FF pollution, in addition to the welfare benefits of ultimately avoiding the more that 9 million current fatalities from outdoor air pollution alone and the associated morbidity. In addition, of course, the benefits from rapid action to avert irreversible climate change and a resulting 'hothouse earth' are essentially incalculable, the ultimate bonus to follow all the co-benefits of energy transition in the short to medium term. The crucial unanswered question for our future remains – will increasingly frequent and severe, climate-related disasters help to overcome denial, disseminate scientific understanding and mobilise public opinion and political will rapidly enough for effective action?

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What we need to know about the pace of decarbonization

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Abstract. Proper recognition of energetic, engineering and economic realities means that the decarbonization of global energy supply will be much more difficult and it will take much longer than is often assumed by uncritical proponents of “green” solutions.

Energy transitions have been among the key defining processes of human evolution (Smil 2017a). The first (millennia-long) transition was from the reliance on traditional biofuels (wood, charcoal, crop residues) and animate prime movers (human and animal muscles) to increasingly common reliance on inanimate energy converters (water wheels, wind mills) and on better harnessed draft animals for fieldwork and in transportation. Transition to fossil fuels (burned to produce heat, thermal electricity and kinetic energy) began in England already during the 16th century but it took off in Europe and North America only after 1800, and in most of Asia only after 1950. This transition has been accompanied by increasing reliance on primary electricity (dominated by thermal electricity since the 1880s, with nuclear generation contributing since the late 1950s).

Post-1800 transition from traditional biofuels to fossil fuels has resulted in gradual relative decarbonization but in enormous growth in absolute emissions of CO_2. Relative decarbonization is best traced by the rising H:C (hydrogen to carbon) ratios of major fuels: they rise from no more than 0.5 for wood and 1.0 for coal to 1.8 for the lightest refined fuels (gasoline and kerosene) and, obviously, to 4.0 for methane (CH_4), the dominant constituent of natural gas (Smil 2017b). The reverse order applies to CO_2 emissions per unit of energy: combustion of natural gas produces less than 60 kilograms of CO_2 per gigajoule (kg CO_2/GJ) while the rates for liquid hydrocarbons are between 70-75. As the global energy transition progressed, coal consumption overtook the burning of traditional biofuels and it was, in turn, overtaken by the combined mass of hydrocarbons (crude oils and natural gases) and rising share of primary electricity has further reduced the average carbon intensity of the world’s primary energy supply. The global mean declined from nearly 28 kilograms of carbon per gigajoule (kg C/GJ) in 1900 to about 25 kg C/GJ in 1950 and then to less than 20 kg C/GJ by 2015. But this relative decline has been accompanied by an almost uninterrupted growth of absolute CO_2 emissions. Combustion of fossil fuels contributed just 8 million tonnes of carbon (Mt C) in 1800 (for CO_2 multiply these totals by 3.667), 534 Mt C in 1900, 6.77 Gt in 2000 and 9.14 billion tonnes (Gt) C in 2018 (Boden et al. 2017; IEA 2019). These emissions have been the principal reason for the rising atmospheric concentration of CO_2, from 285 parts per million (ppm) in 1850 to 369.6 ppm in the year 2000 and to 408.5 ppm in 2018 (NASA 2019a; NOAA 2019). In turn, these rising concentrations have been the principal reason for gradual increase of average tropospheric temperature that has, so far, amounted to about 0.8^0 C (NASA 2019b) but that would, in the absence of any remedial actions, surpass 2^0 C or even 3^0 C in a matter of decades and result in rapid anthropogenic global warming (IPCC 2014).

Past transitions were driven by a variety of factors ranging from the need for higher unit power (even small water wheels were more powerful than an ox or a horse) and better conversion efficiency (windmills can lift irrigation water much more efficiently than people) to more affordable supply (heating coal was far cheaper than charcoal) and reduced environmental impacts (natural gas is a much cleaner fuel than coal). In contrast to previous energy transitions the unfolding quest for decarbonization is not primarily driven by resource shortages or technical imperatives (most of the existing conversions are highly efficient and also very reliable). Today's quest for decarbonization has one dominant goal: limiting the extent of global warming. The goal is to establish a new global energy system devoid of any combustion of carbon-containing fuels or the world with net-zero carbon emissions where a limited amount of fossil fuel combustion would be negated by the removal and sequestration of the gas from the atmosphere resulting in no additional carbon releases.

How have we done so far? Concerns about anthropogenic global warming (a phenomenon whose basic cause has been appreciated since the late 19th century) began to receive wider public attention during the 1980s, and the first United Nations Framework Convention on Climate Change was signed in 1992 (UNFCCC 1992). It was followed by the Kyoto Protocol of 1997 and its latest global endeavor was the 2015 Paris Agreement that included nationally determined contributions designed "to combat climate change and to accelerate and intensify the actions and investments needed for a sustainable low carbon future" (UNCC 2019). Numerous meetings and assorted pledges aside, what has actually taken place since 1992?

The most important fact is that during those decades of rising concerns about global warming the world has been running into fossil carbon, not moving away from it. Since 1992 absolute emissions of CO_2 from fossil fuel combustion have declined significantly (by nearly 20%) in the EU28 and have grown only marginally (in each case by about 5%) in the US and Japan (Boden et al. 2017) but these accomplishments have not set the world on the road to decarbonization as emissions have nearly tripled in Asia, largely because the Chinese combustion of fossil fuels has almost quadrupled (Boden et al. 2017; PBL 2018). As a result, global emissions of CO_2 increased by more than 60% since 1992, setting yet another record in 2018.

Historians of energy transitions are not surprised by this development, as history shows that neither the dominant sources of primary energy nor the common energy converters can be displaced rapidly and completely in short periods of time. The high degree of the global dependence on fossil carbon and the enormous scale of the fuel-dominated global energy system mean that the unfolding energy transition will inevitably follow the progress of all previous large-scale primary energy shifts and that it will be a gradual, prolonged affair (Smil 2017a). In 1800 traditional biomass fuels (wood, charcoal, crop residues, dung) supplied all but a tiny share of the world's primary energy, a century later their share was about 50%, and at the beginning of the 21st century they still accounted for nearly 10%. This means that even after more than two centuries the world has not completed the shift from traditional biofuels to modern sources of primary energy.

Coal's share of global primary energy supply has been in retreat for generations as the reliance on hydrocarbons has grown – but the fuel still supplies nearly 30% of the total requirement. That is still more than natural gas (whose commercial extraction began about 150 years ago but whose share of total supply has been growing slower than expected) and in absolute terms its output is more than eight times larger than it was in 1900 when the fuel dominated the global energy supply. And while most economies began to reduce their reliance on crude oil in the aftermath of OPEC's two rounds of large price increases during the 1970s, the fuel remains the dominant source of the world's primary energy, supplying nearly 40% of the total.

The unfolding transition toward non-carbon energies has to take place on unprecedented scales. Annual extraction of fossil fuels now includes about 7.7 Gt of coal, 4,4 Gt of crude oil and 3.7 trillion cubic meters of natural gas, altogether an equivalent of nearly 9 Gt of crude oil or about 370 EJ (BP 2018). This grand total is the flux that matters: unlike all other previous shifts in primary energy use, the unfolding decarbonization can achieve its goal – eventual elimination of fossil carbon – only when it succeeds on the global scale. Substantial decline of carbon emissions, even an instant decarbonization of energy supply in a major advanced economy, makes little difference as long as the greenhouse gas emissions from other sources and from other countries keep on rising.

Even after some three decades since the beginning of high-level global warming concerns the unfolding transition is still in its earliest stage and even the relative shift has been, so far, minor. When the shares of primary energy are calculated by excluding traditional biofuels and by converting all non-thermal primary electricity by using its energy equivalent (1 Wh=3,600 J), fossil fuels supplied 91.3% of the world's primary energy in 1990 and by 2017 their share was still 90.4%. As with many phenomena in early stages of expansion, the combined growth of contributions made by new renewables (wind and solar electricity generation and modern biofuels) has been rapid: in the year 2000 they supplied only about 0.2% of the global primary energy supply, their share reached 1.3% by 2010 and 2.2% by 2017 – but that was still well behind the contributions made by either hydro and nuclear generation.

Of course, the shares of new renewables are significantly higher for electricity generation because this sector has been the main focus of the unfolding drive for decarbonization. Photovoltaic cells and wind turbines generated a mere 0.2% of the world's electricity in the year 2000, the share reached 4.5% in 2015 and nearly 7% in 2018 (BP 2018). But even if the decarbonization of global electricity generation were to proceed at an unprecedented pace, only the availability of affordable, massive-scale electricity storage would make it possible to envisage a reliable system that could rely solely on intermittent renewable energies of solar radiation and wind. Even securing just three days-worth of storage for a megacity of more than 10 million people that would be cut off from its intermittent renewable sources (a common occurrence during the monsoonal season in Asia with heavily overcast skies and high winds) would be prohibitively expensive by using today's commercial batteries.

Setting aside exaggerated media claims, a technological breakthrough meeting that requirement appears unlikely in the near future as pumped hydro storage (originally introduced during the 1890s) remains today the only way to store electricity at gigawatt scale. And even major advances toward large-scale electricity storage would not be enough to bring about rapid decarbonization of the global energy supply as electricity generation accounts for no more than 20% of total final energy consumption, and as decarbonizing transportation, heating, agriculture and industrial production is considerably more difficult than installing new intermittent capacities, connecting them with major load centers and securing the required back-up supply.

Electrification of passenger cars is in its earliest stage, with 5.4 million electric vehicles on the road by the end of 2018, still less than 0.2% of all vehicles registered worldwide (Insideeves 2019). More than a century after they were first seen as the best road transportation choice, electric cars are finally ascendant, but even under the best circumstances it will take many decades to accomplish the transition from internal combustion engines. The International Energy Agency sees 160-200 million electric vehicles by 2030, BP expects 320 million by 2040 and my best forecast (based on a polynomial regression) is for 360 million in 2040 (IEA 2018; BP 2019). But by that time there might be about 2 billion vehicles on the road globally (compared to about 1.25 billion today), and hence even 400 million electric cars would be just 20% of the total. Forecasting the future adoption of hydrogen-fueled vehicles is even more uncertain, but it is hard to see how even the most likely combined progression of electric and hydrogen cars would completely eliminate internal combustion engines before 2040, or even soon after.

Given the energy density of today's best commercial batteries, the electrification of trucking, shipping and flying is even more challenging. The key to understanding the fundamental difficulty is to compare the energy densities of the best Li-ion batteries with the energy density of diesel fuels used in trucking and shipping. Today's widely deployed Li-on batteries have an energy density of up to 260 Wh/kg, and it is foreseen that they could reach up to 500 Wh/kg in the future (J.P.Morgan 2019). In contrast, diesel fuel used in land and marine transport and aviation kerosene have, respectively, energy densities of 12,600 Wh/kg and 12,800 Wh/kg), which means that today's dominant liquid transportation fuels are nearly 50 times as energy dense as our best commercial batteries - and this gap is not to be closed anytime soon. Shipping and flying present particularly insurmountable challenges as only high energy density fuels can power massive container ships carrying more than 20,000 steel units on their long intercontinental routes (Smil 2019) and high-capacity commercial airliners.

While air conditioning is powered by electricity, seasonal heating in cold parts of Eurasia and North America now relies overwhelmingly on natural gas delivered by large-diameter trunk lines and dense networks of small-diameter distribution lines serving more than half a billion customers. Obviously, replacing this fuel supply and abandoning this extensive infrastructure will not be achieved over a single generation. And even more intractable challenges come with the decarbonization of industries producing what I have called the four pillars of modern civilization: ammonia, cement, steel and plastics (J.P. Morgan 2019).

Mass-scale production of these materials (annual outputs are now close to 200 Mt for ammonia, about 4.5 Gt for cement, 1.6 Gt for steel ad about 300 Mt for all kinds of plastics) now depends on large-scale inputs of fossil fuels, both for process heat and as feedstocks. Without Haber-Bosch synthesis of ammonia (with natural gas as the dominant feedstock and fuel), nearly half of today's humanity would not be alive as even the most assiduous recycling of all available organic matter could not supply enough nitrogen to feed nearly 8 billion people. Cement and steel are the two irreplaceable infrastructural components. Cement is produced in kilns heated by low-quality fossil fuels, two-thirds of all steel are made in basic oxygen furnaces from pig iron that is smelted in blast furnaces with the aid of about one billion tonnes of coke, augmented by natural gas (Smil 2016). And gaseous and liquid hydrocarbons are the dominant feedstocks (and fuel) for synthesizing a wide variety of plastics.

All of these processes have one important characteristic in common: there is no available non-carbon alternatives that could be readily deployed on mass commercial scales. There are some interesting innovations, and entirely new pathways might be possible – ranging from new catalyses for ammonia synthesis (Ashida et al. 2019) to hydrogen-based steelmaking (Green 2018) – but none of these innovations has been deployed even as pilot plant experiments and, once again, it is obvious that scaling up those processes that may eventually prove acceptable in order to reach annual outputs of hundreds of millions, even billions, of tonnes is a task that would take generations to accomplish.

Yet another important factor to consider are the enormous energy, food and material needs of emerging economies. China's post-1990 surge in demand for these inputs indicates the extent of future needs. China's population of 1.39 billion people will be soon surpassed by India – whose per capita energy use is only about a quarter of the Chinese level (BP 2018) – and between 2015 and 2050 1.3 billion people will be added in Africa where per capita use is generally well below the Indian level. Much like China has done by more than quadrupling its fossil energy use since 1990, these populous modernizing countries or regions will use any available source of energy to raise their standard of living and to build their essential infrastructures. Not surprisingly, India's total primary energy consumption is forecasted to increase nearly five-fold between 2012 and 2047 according to a recent study by the National Institution for Transforming India (NITI Aayog), and coal is expected to remain its dominant fuel (Thambi et al. 2018).

In conclusion, the verdict – based on the history of past energy transitions, on the unprecedented scales of the unfolding shift, on the limits of alternative pathways, and on the enormous and immediate energy needs of billions of people in low-income countries – is clear. Designing hypothetical roadmaps outlining complete elimination of fossil carbon from the global energy supply by 2050 (Jacobson et al. 2017) is nothing but an exercise in wishful thinking that ignores fundamental physical realities. And it is no less unrealistic to propose legislation claiming that such a shift can be accomplished in the US by 2030 (Ocasio-Cortez 2019). Such claims are simply too extreme to be defended as aspirational. The complete decarbonization of the global energy supply will be an extremely challenging undertaking of an unprecedented scale and complexity that will not be accomplished – even in the case of sustained, dedicated and extraordinarily costly commitment – in a matter of few decades.

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Battery Electric Vehicles: Perspectives and Challenges

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Abstract. In the early decades of the car industry (1880-1920), battery electric vehicles (BEVs) got a remarkable popularity. Eventually, they fell into oblivion for nearly a century, leaving the stage to internal combustion vehicles (ICVs), which enabled long-distance driving thanks to the superior energy density of liquid fuels. The invention of the lithium-ion battery (LIB, 1991), characterized by unprecedented energy density and steeply decreasing costs, set the stage to reverse this century-long trend, making nowadays BEVs a competitive alternative to ICVs. In this paper, we analyze the perspectives of battery electric cars, quantitively assessing their performance in terms of energy efficiency and consumption versus ICV counterparts. An examination of material requirements for manufacturing each battery component is made, with focus on critical resources such as cobalt, dysprosium, lithium and graphite. Based on quantitative data, we conclude that the transition to electric powertrains for light-duty vehicles is not only desirable but also doable. However, this must be accomplished by following circular economy principles across the whole industrial chain, in the frame of a wider, radical transformation of the mobility system towards more sustainable models.

Keywords. Battery electric vehicles, lithium ion batteries, cobalt, dysprosium, critical materials, energy efficiency, circular economy.

THE RISE, FALL AND REBIRTH OF THE ELECTRIC CAR

The widespread notion that electric cars are a new technological concept is incorrect. The first battery-powered electric vehicle (EV) was made in 1834, *i.e.*, over 50 years before the first internal combustion vehicle (ICV) powered by gasoline went onroad.[1] Notably, the first examples of machines for personal transportation were based on steam engines and dates back to the very beginning of the 19th century. A century later, at the turn of the 20th century, the share of registered US cars was as follows: 40% powered by steam, 38% by electricity, 22% by gasoline (Figure 1).[1] Therefore, as weird as it may sound nowadays, the fight for predominance among the three car concepts was far from over in 1900, when refined oil products were still scarcely available, electricity was a luxury for (some) city dwellers, and roads were far from being developed and paved outside the main urban centers.

Figure 1. From left to right, examples of electric, steam and internal combustion engine cars of the early 20th century (1906, 1908, 1925, respectively).

In the early 20th century, cars were only used by wealthy people within metropolitan areas, where distances were very short. This is why electric cars were still an attractive option. Moreover, EVs were silent, did not produce any smoke or smell and – most remarkably – did not require hand crank to be turned on. However, within a few years, the situation dramatically changed in favor of ICVs,[2] whose dominance in road transportation was poised to last for over one century. The main drivers for the triumph of ICVs were (i) the invention of the electric starter in 1912, (ii) the start of the industrial production of the Ford Model T in 1908 (though Henry Ford continued to use his luxury electric car); (iii) the oil boom in Texas that made gasoline increasingly available at affordable prices, (iv) the development of road networks that required cars with increasingly long mileage.[2] The last EV of the pioneering times was produced in Detroit in 1926[1] and the idea was (ephemerally) resurrected only in the 1970s in the aftermath of the first oil crisis. Waves of interest occurred in the last part of the 20th century, but times were not mature, primarily because battery technologies (typically based on lead-acid systems) were not capable of providing acceptable mileage at an affordable price and overall weight.

In 1997 Toyota released Prius, the first hybrid car (Figure 2).[3] It combined an ICE with electric propulsion, which enabled a decrease of fuel consumption in urban settings. Nowadays, hybrid cars are the preferred choice for taxi drivers in many cities worldwide. The success of Prius and of some other hybrid models (almost exclusively from Japanese firms) marked the slow rebirth of electric mobility. The first Prius used a nickel-metal hydride (NiMH) battery pack.[4]

The technological game changer that made at last possible the dream of Thomas Edison – the pioneer of the electric transportation – is the rechargeable lithium-ion battery (LIB), which was introduced in the market by Sony corporation in 1991 to power laptops.[5,6] The progressive introduction of portable devices on a large scale (mp3 players, mobile phones, etc.) and also of systems requiring bigger battery packs (home appliances, bikes) offered a formidable opportunity to boost the development of LIBs and widely expand the market. This trend was timely pinpointed by two American engineers, Martin Eberhard and Mark Tarpenning, who realized that LIBs could be the long-awaited solution to enable battery vehicles with long ranges. They founded Tesla Motors in 2003 and were soon joined by Elon Musk, a flamboyant South African immigrant and entrepreneur, who became the CEO and product architect of the company. Since then, Tesla has become one of the most noteworthy, controversial and debated companies in the world. Whatever will be its future destiny it will be historically remembered as the company which challenged the most gigantic industrial conglomerate of human industry – oil & automotive – and forced it to change its century-old trajectory.[7]

There are three types of cars equipped with a battery pack: hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and battery electric vehicles (BEVs). HEV batteries are charged only by the thermal engine or via regenerative braking, whereas in PHEV these processes can be integrated by direct charging on the electric grid. BEV have only an electric motor and can be powered exclusively by electricity. This article will primarily deal with BEVs, often indicated simply as electric vehicles (EVs).

THE KEY COMPONENTS OF BATTERY ELECTRIC VEHICLES

BEVs are easier to assemble and cheaper to maintain than ICVs simply because they contain a much smaller number of moving parts.[8] Hybrid, instead, are by far the most complex and materials intensive automobiles, as

Figure 2. The slow rebirth of electric vehicles: the first hybrid Toyota Prius (1997, top) and the Tesla Roadster (2008, bottom).

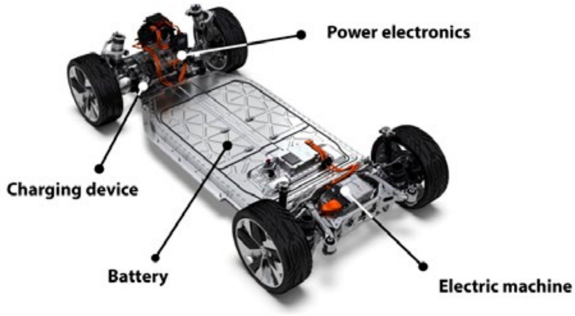

Figure 3. The key components of a battery electric vehicle (BEV).

they contain both electric and traditional components. Key constituents of BEVs are: the battery, the electric machine, the power electronics and the charging device.[9] A schematic representation of the key components of an electric car are depicted in Figure 3.

Battery. It determines the key technical attributes of an EV, such as driving range and also performance. In the past, EVs were equipped with lead-acid or nickel hydride batteries, but nowadays lithium ion batteries (LIBs, see also next paragraph) are by far the dominant technology and their role is not expected to fade even in the medium-long term, due to the unique (electro)chemical and physical properties of lithium.[6] The most important parameters that define the quality of a battery are the mass and volume energy densities, the former being expressed in MJ/kg (or more often in Wh/kg and indicated as "specific energy") and the latter in MJ/L or Wh/L;[10] the volume energy density is particularly relevant for vehicles, due to obvious space constraints. In Figure 4 are depicted energy densities of some types of batteries, along with those of the liquid fuels used in transportation. It must be emphasized that data in Figure 4 refer to *cells*, but car batteries operate as *packs*. These include the control circuitry that warrants the car performance under any conditions and the robust casing that protects the cells (vide infra). Therefore, at pack level, the battery energy density is smaller by 30-50% compared to bare cells. On the long term, the accessory parts of the battery appear to be the main limit for increasing energy density. The energy density of the most performing LIBs for EVs are presently close to 250 Wh/kg (Tesla Model 3), or 710 Wh/L.[11] This value unfavorably compares with gasoline or diesel fuels, which is nearly 15-fold higher at ca. 10,000 Wh/L. However, this comparison is partly misleading because the energy packed in the storage unit must be converted into mechanical movement. For this job an electrical motor is 3-4 times more efficient than a combustion engine and, at the same time, is substantially lighter. Therefore, power densities should be normalized accordingly.[12] A 75 kWh lithium ion battery pack (Tesla Model 3) weights about 478 kg, whereas an equivalent ICE car requires the burning of only 25 kg of gasoline to deliver the same energy to the wheels.[4] However, it must be emphasized that an EV is a closed

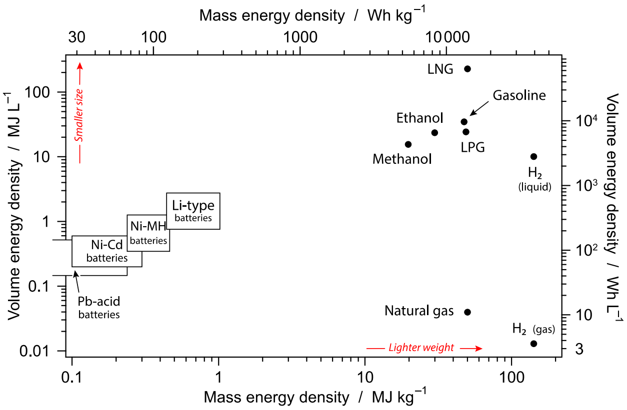

Figure 4. Volume and mass energy densities of some selected batteries and liquid fuels. Both MJ and Wh are reported in the diagram as energy units (on opposite sides), as both are largely diffused in the literature and technical documents.

system which exchanges only (electric) energy with the external environment, whereas ICVs are open systems undergoing a constant inbound flow of fuels and an outbound flux of gaseous chemicals at tailpipe. After 250,000 km, an average diesel car running at 18 km/L, has burnt 13,900 L of fuel, i.e., over 10 tons corresponding to about 8 times the weight of the whole ICE car and over 20 times the weight of a 75 kWh EV battery. When the electricity is produced by solar panels (an increasingly frequent case) the flux of matter that moves an electric car is reduced to zero across the entire supply chain. In other words, comparisons of energy density and material intensity of batteries vs. traditional fuels is less straightforward than it may appear at first sight.

Electric machine. This term defines the combination of the electric motor, converting the electrical in mechanical energy, and the power generator coupled to it, which recovers kinetic energy from braking and deceleration and convert it into electricity for recharging the battery. Electric machines are characterized by an high starting torque (up to 1,000 Nm), high efficiency (up to over 90% battery-to-wheels), robustness, negligible noise, long life and low maintenance costs. Electric machines can run with both direct (DC) and alternating (AC) current. Traditionally, series wound DC motors have been used, but today modern BEVs can also be powered by AC. The alternating current generates a rotating magnetic field that causes rotational movement inside the motor (made up by a stator and a rotor) via electromagnetic induction. In turn, the motor is coupled to a gearbox that brings the power directly to the wheels; the speed of the vehicle depends on the Pulse Width Modulation (PWM) frequency of the power converter. In principle, in a BEV, the electric motor can be directly incorporated into the wheel (as e.g., in the Michelin Active Wheel), removing the need for a complex and intrinsically inefficient transmission system of ICVs that converts the linear and noisy motion of cylinders into the circular motion of the wheels.

Power electronics. The power electronic module oversees all the functions that control the efficiency and economy of the vehicle, such as torque and efficiency of the motor, and regeneration of the battery charge. The main function is to convert the DC output of the battery into an AC feed for the motor through an inverter (or viceversa during recuperation). It also controls the different levels of voltage, depending on the power demand and specific device to run. It is also very important for the charging process.

Charging device. It is the interface between the vehicle and the electric grid. Modern electric cars can be typically charged both with AC and DC. The AC charging mode is controlled via an onboard system which operates during slow garage-based operations (2-3 kW, standard socket) or in small-medium size recharging stations up to 22 kW. If one wants to charge faster, the AC/DC converter needs to be bigger and heavier, taking up more space and increasing the complexity and cost of the vehicle. Therefore, off-board DC fast-charging systems are typically used to charge the battery with higher power (≥ 50 kW).[4] Fast DC charging stations up to 300 kW are now being introduced by some companies. This poses relevant challenges for the long-term integrity of the battery (a very efficient cooling systems is required) and for the electric grid as a whole. In fact, with a high market penetration of BEVs, the stability of the grid may in principle be endangered not only by extensive networks of high-power fast charging stations with high peak demands,[13] but also by uncoordinated EV charging at the residential level at low-medium power.[14] Accordingly, the diffusion of the electric car must be accompanied by an upgrade and strengthening of the electric grid, i.e., the so-called smart grid.[15] In this scenario, a large share of electric vehicles should be ideally charged around midday, when the peak of photovoltaic production occurs. This can be facilitated by a larger diffusion of parking lots equipped with charging stations at workplaces.

THE CORE OF BEVS: THE LITHIUM ION BATTERY

The basic idea of this device (whose concept dates back to 1970s)[6] is the reversible, alternate intercalation of Li^+ in a lithium oxide material at the cathode and in graphite at the anode, upon redox processes. J. B. Goodenough, M. S. Whittingham and A. Yoshino were awarded the Nobel Prize in Chemistry 2019 for the development of lithium-ion batteries.

Lithium is the smallest and lightest metal ion, hence LIBs exhibit intrinsically high mass energy density and are particularly suitable for fast recharging. Moreover, it has excellent cycling performance and exhibits one of the highest electrochemical potential among metals, which enables devices with high voltage. A LIB is made of anode, cathode, separator, electrolyte and two metallic current collectors at each terminal; it is schematically depicted in Figure 5.

Upon battery charging, the Li^+ ions are forced to move away from the cathode (where cobalt/nichel oxidation occurs) and nest inside the graphite layers (which gets reduced) of the anode; upon discharging, they go back to the cathode at their equilibrium position. In

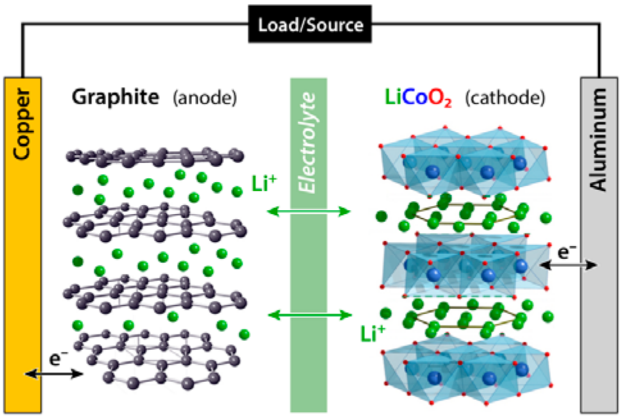

Figure 5. Scheme of a lithium ion battery, where Co^{4+}/Co^{3+} half reaction occurs at the cathode and redox-promoted intercalation of lithium in graphite takes place at the anode.

parallel, electrons move back and forth along the external circuit and are conveyed to the Al and Cu terminals on the cathode and anode side, respectively. Upon battery discharge, the electric current powers the external device. When shuttling between electrodes, Li^+ ions passes through a plastic polymer separator that prevents the flow of electrons inside the battery.

The cathode of LIBs is made of layered oxides of general formula $LiMO_2$, where M indicates some combination of Co, Ni, Al, and Mn; nowadays anodes are made of carbonaceous materials, particularly natural and artificial graphites.[16] Non-layered cathodes can be made of less precious Li oxide materials (e.g., $LiFePO_4$), but their energy density is not comparable with layered systems and cannot be used in highly performing LIBs. The electrolyte is typically a lithium salt in an organic solvent or gel. The replacement of the latter media with solid matrices would be a substantial breakthrough of the LIB technology, particularly in terms of durability and safety.[17]

The features of the three main families of LIBs currently on the market are reported in Table 1. Cobalt is omnipresent, due to the unique electronic configuration of Co^{3+} with 6d electrons in a low spin state, which makes it particularly small and capable of affording batteries with high energy density. Big efforts are being made to reduce as much as possible the cobalt content, due to supply concerns (vide infra). For instance, the Nichel-Manganese-Cobalt batteries (NMC) have progressively evolved as, for instance, NMC111, NMC622 and then NMC811, where the numbers designate the specific ratio of each metal.[18]

The element requirements of some common electrodes (in kg/kWh) are reported in Table 2.[18] From these data it can be inferred that a medium sized 40 kWh battery NMC 111 contains in the cathode about 5.5 kg of Lithium (without considering the electrolyte), 15.7 kg of Ni, 14.7 kg of Mn and 15.8 kg of Co (to be reduced to 8.6 and 3.8 kg with NMC 622 and NMC811, respectively). A battery of a 40 kWh BEV also contains nearly 50 kg of graphite, irrespective of the cathode composition. Efforts to increase the energy density of batteries are now also addressed to the improvement of the standard graphite anode, with focus of silicon-based materials.[20] These solutions are still far from large-scale market applications.

Real-life batteries for electric vehicles are made of hundreds or thousands of individual cells having the structure depicted in Figure 5 and connected in a series and parallel combination. These cells may have three different shapes: cylindrical, prismatic and pouch, the latter being characterized by very small thickness (< 1 cm). Different car manufacturers adopt different types of cells and related assemblies (Figure 6).

Tesla uses cylindrical cells slightly longer and wider than conventional AA cells for home appliances, profiting from the large manufacturing experience of its part-

Table 1. Key parameters and applications of the three main families of LIBs.[19]

Name	Battery type		
	Lithium Cobalt Oxide (LCO)	Lithium Nickel Cobalt Aluminum Oxide (NCA)	Lithium Nickel Manganese Cobalt Oxide (NMC)
Cathode	$LiCoO_2$	$LiNiCoAlO_2$	$LiNiMnCoO_2$
Voltage [V]	3.7 – 3.9	3.65	3.8 – 4.0
Mass energy density [Wh kg^{-1}]	150 – 240	200 – 300	150 – 220
Cycle life	500 – 1000	500	1000 – 2000
Thermal runaway [°C]	150	150	210
Applications	Mobile phones, tablets, laptops, cameras.	Medical devices, electric powertrains, industrial.	E-bikes, medical devices, electric vehicles, industrial.

Table 2. Li, Co, Ni, Mn, Al requirements for common battery cathodes (kg/kWh).[18]

	Li	Co	Ni	Mn	C
LCO	0.113	0.959	–	–	≈ 1.2
NCA	0.112	0.143	0.759	–	
NMC111	0.139	0.394	0.392	0.367	
NMC622	0.126	0.214	0.641	0.200	
NMC811	0.111	0.094	0.750	0.088	

ner Panasonic, with whom it has developed the so called Gigafactory 1 in the Nevada desert. This enormous facility is planned to be energy self-reliant through a combination of photovoltaic, wind and geothermal energy. The projected capacity for 2020 amounts to 35 GWh/y of automobile cells and 50 GWh/y of battery packs for stationary backup of renewable power facilities, but it is not yet evident if these targets will be fully met. The idea is to demonstrate cradle-to-cradle handling of Lithium ion batteries, all the way from raw materials to manufacturing and then recycling. The battery pack of the long-range Tesla Model 3 (75 kWh) contains 4416 cylindric batteries (70 mm length, 21 mm diameter; 66 g) arranged in 96 blocks of 46 parallel connected cells. The Nissan leaf 2018 (40 kWh), has a battery pack made of 24 modules, each containing 8 pouch NMC cells. Each of these 296 cells weights 914 g and have a size of 261x216x8 mm. All the battery packs in BEVs are protected by robust metallic and plastic enclosures that protect the cells from external elements (e.g., dust, moisture, rain, debris) and must withstand severe crash tests to warrant the safety of passengers in case of accidents.[21] Last but not least, BEVs are equipped with a battery management system (BMS) which warrants integrity and best performance, for instance by avoiding damages due to anomalies in temperature or electricity supply.

Figure 6. Individual cells for BEVs and their final assembly in the pack: Tesla (cylindrical, top) and Nissan Leaf (puch, bottom).

Nowadays battery packs range typically from 20 up to 90 kWh; the driving range is rated between 150 and 500 km,[16] but strongly depends on the weight of the vehicle, style of driving, speed and, quite remarkably, outside temperature.[22] At 0 °C the mileage of an EV is shortened by about 30% and even more in harsher winter conditions, this is related to a lower intrinsic efficiency of the device at low temperature and to the energy needed to warm up the car interior. Also hot temperatures have detrimental effects for similar (and opposite) reasons, but to a substantially lesser extent. As far as temperature is concerned, one may say that LIBs are like human beings: they perform best in the range 15-30 °C.[22] (4) Average consumptions of EVs are about 12-14 kWh/100 km in mild and warm seasons and 15-17 kWh/100 km in cold weather.

Present targets for BEVs to become fully competitive with conventional thermal cars concern:

(i) *Faster charging capabilities* in order to achieve 80% state of charge within 5-20 min. This target will become more challenging if the average battery capacity will grow bigger. For example, to charge a 60 kWh battery (350-400 km range) in 20 min would require at least 180 kW of charging power and a very efficient on-board temperature control management of the cells. Nowadays standard fast charging stations are normally rated 50 kW. It must be emphasized again that the diffusion of fast charging stations requires a more rational management of electricity peak demand, to be ideally matched with the daily and seasonal production peaks of renewable electricity.

(ii) *Higher battery energy density* at about 240 Wh/kg and 500 Wh/L at pack level, in order to routinely reach driving ranges of 500 km.[16] This is technically possible already, but only for models which, at present, are economically accessible to a limited fraction of consumers.

(iii) *Price decrease* down to 125 \$/kWh at pack level to become fully competitive with ICVs at the car showroom. Present battery costs are placed at 100–170 \$/kWh and 220–250 \$/kWh at the cell and pack level, respectively.[16]

Regarding future perspectives, research on next generation batteries targets the development of new sensors to monitor complex reactions in the device, so as to enable self-healing and enhance battery performance and lifetime.[23]

CRITICAL RAW MATERIALS IN BEVS

Since 2011 the European Commission has compiled a list of "critical raw materials" (CRM); the latest list has been issued in 2017 and contains 27 materials or classes of materials such as Platinum Group Metals (PGM) or Rare Earth Elements (REE).[24] Materials are defined critical after a thorough screening that quantitatively assesses (i) importance for the EU economy in terms of end-use applications and added value and (ii) risk of supply disruption for the EU.

Due to the ever-increasing number of road vehicles worldwide, the huge size of the market and the extensive use of materials of different sorts in automobiles (a light-weight duty vehicle weights between 1 and 3 tons) the car industry is the object of intensive studies to assess its materials sustainability.[25] This issue is even more important nowadays, because this industrial sector is undergoing a technological shift from thermal to electric traction.

The body and some auxiliary parts of BEVs and ICVs are virtually identical. The electric machine is much lighter than the conventional combustion engine, but this advantage is counterbalanced by the heavy battery pack, which can exceed 600 kg for the largest capacities (85-100 kWh).[26] The weight of battery packs is almost linearly correlated with overall capacity, when the same cell technology is examined. On the other hand, ICVs have a much larger number of parts, which impacts the mass of the automobile. All in all, BEVs equipped with lithium ion batteries and ICVs of comparable size have a similar weight, but BEVs are more material intensive than conventional thermal cars. In other words, they contain substantial amounts of more "sophisticated" materials (particularly metals) some of which are considered critical.[27] In Figure 7, major raw materials utilized in electric cars are schematically indicated.[27]

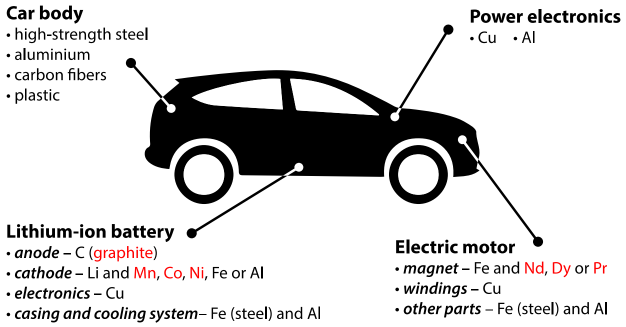

Figure 7. Most relevant materials used in different parts of battery electric vehicles. Those defined as critical are highlighted in red.

As far as material criticality is concerned, battery is by far the most sensitive part of BEVs, both in terms of number of materials involved and quantity utilized.[18,27] As pointed out above, the battery pack of a BEV contain some tens of kilograms of metals – in particular Li, Co, Ni, Mn and Al (cathodes, electrolyte) – and graphite materials (anode). In batteries, Cu is only used as anode collector (along with Al on the cathode) in rather limited quantities. However, Cu is a strategic metal for the electric mobility system as a whole, being widely employed in car circuitry and wiring, all the way to the electric grid.

Among the materials listed in Figure 7, Co, Li, Dy are the most critical in terms of potential availability risks, whereas graphite is critical because the production is highly concentrated in one country (China). Let us briefly examine each of them.

• *Lithium.* At present, lithium is the most difficult component to replace in BEVs. Its mass, volume and electrochemical properties suggest that the role of lithium in this sector can be reduced only going beyond metal-based batteries, an unlikely scenario for the foreseeable future.

In 2017, about two thirds of lithium was extracted from hard rocks,[28] which are crushed to allow the separation and concentrations of lithium minerals and then chemically processed (e.g., by leaching) to obtain lithium hydroxide, carbonate or chloride. An easier, cheaper, but longer process is extracting lithium dissolved in highly concentrated underground saltwater solutions called continental brines. Such brines are brought to the surface by drilling wells and then moved through a series of surface ponds to concentrate the lithium salts and remove impurities (Figure 8). The last step is chemical treatment to make the final marketable product, such as dry lithium carbonate.[28] Extraction from brine was started in the salt lakes of the Atacama desert in

Figure 8. Lithium brine ponds in the Lithium Triangle, South America (bottom right map).

Chile in 1980s. This technique is now dominant in the so-called "Lithium Triangle", the region between Chile, Bolivia and Argentina where the concomitance of geological, orographic and climate conditions have created several lakes very rich in lithium brines (Figure 8). The largest lithium reserve in the world is the Salar de Uyuni in Bolivia, for which extraction plans are conflicting with the need to preserve a place of unique environmental value and are challenged by the presence of high concentrations of magnesium, which needs to be separated.[29] It has to be emphasized that lithium extraction from brines, though relatively easy, is a lengthy process that cannot quickly respond to the steep rises in demand that are expected in the years to come.[27]

According to the US Geological Survey (USGS), Australia (from hard rocks) and Chile (from brines) currently dominate lithium production with 60% and 31% of global output in 2018, respectively.[30] The production of this highly valuable metal has been on a steep rise in recent years (+ 23% in 2018), due to enhanced demand for all types of electric vehicles. The largest known untapped resources (i.e., identified deposits) are concentrated in the Lithium Triangle, but their upgrade to reserves (i.e., technically and economically exploitable stocks) is still uncertain in Bolivia and Argentina.[28] The search for new lithium reserves is a relatively recent trend, hence it is reasonable to expect the discovery of relevant deposits in new geographic areas such as Afghanistan, where effective exploitation may be extremely challenging for a variety of technical and political issues.[31]

In 2018, over 80 million new cars were sold. On the other hand, we can approximately assume that an average BEV contains about 10 kg of lithium in the battery.[32] Therefore, if all the cars presently sold worldwide were BEVs, the annual lithium demand would be 800,000 tons. This is about 10 times the current world production,[30] half of which goes to the battery market, the rest being used in ceramics, glass, lubricants and other minor applications.[28] These data also suggest that the present production of lithium for the manufacturing of batteries (about 40,000 tons/y) can in principle sustain only a 5% share of EV in the present global annual car market.

The substantial increase in resource and reserve estimates in recent years does not indicate risks of lithium shortages up to the medium term (10-20 years).[18] Recently, there have been a supply deficit for refined products and an oversupply of mined minerals. Spot prices of lithium carbonate have fallen 60% from early 2018 to mid-2019, but long-term contract prices (over 75% of lithium trade globally) were rather stable in the same period. Forecasting on the longer term on such a complex and evolving market is difficult. Price trends depends on multiple factors such as the evolution of the market in road vehicles,[8,33] the availability of new lithium reserves and, last but not least, the establishment of recycling practices in a circular economy perspective. At present, lithium recovery is technically possible through a variety of pyrolytic, hydrothermal as well as pyro- and hydrometallurgic methods.[27] Despite some companies have implemented industrial processes for recycling LIBs,[34] the recovery and recycling of lithium from batteries remains scarcely attractive at the present cost of virgin mineral products.[18] The economic attractiveness of recycling will improve when the number of end-of-life EVs will substantially increase.

LIBs in cars are considered exhausted when they can recharge at 80% of the initial rate, a level allowing excellent performance in some second-life applications such as accumulators for renewable electric generation facilities powered by intermittent sources (wind, photovoltaics). Some companies have implemented this practice in flagship sites such as the Amsterdam stadium (3 MW),[35] showing that car LIBs can fruitfully serve well beyond the performance guaranteed by car manufacturers which is between 150000 and 200000 km. Longer mileages can be achieved by a thorough daily management, especially in the recharging phase.[36] For instance, it is advisable to not keep them above 80% or below 20% of their capacity for very long times. This means that batteries of higher capacity (> 60 KWh) can in principle last longer, as the number charge/discharge cycles across their lifetime tends to be lower.

- *Cobalt.* Cobalt is considered the most serious potential obstacle for the expansion of the LIB market for electric mobility.[18] As already pointed out, cobalt is the best choice among transition metals to get laminated cathodes with very high energy density; so far, it could be only partially substituted with Ni or Mn. In the last decade (2009-2018) the world mine production of cobalt has increased by 125%, from 62 to 140 kton/year;[37] in comparison Ni production has increased by "only" 64%, (from 1.4 to 2.3 Mt).[38] By assuming 10 million BEV cars sold yearly by 2025 (about 10% of the global car market) – with an average battery pack of 75 kWh (about 400 km driving range) and under the assumption of a mixed cathode chemistry relative to the present technologies – the global demand for cobalt in LIBs would increase up to almost 600% (from 50 to 330 kt, 2016-2025).[18] At present, it is not evident if supply can keep up with such a steep demand, in the absence of substantial technological advancements to reduce the use of cobalt in LIBs, even if demand trend will be less disrupting, as projected by other studies.[39]

Besides impending constraints in material availability, cobalt is critical for other aspects. First of all, most of it is obtained as a byproduct of the extraction of Ni and Cu (about 60% of the world cobalt production comes from copper ores),[40] which means that its production is dictated by the market trends of its parent "attractor metals", potentially generating uncertainty and price volatility.[41] Moreover, cobalt production is concentrated (around 60%) in a politically unstable country such as the Democratic Republic of Congo (DRC), where violation of human rights in small uncontrolled mines is well documented.[42] To give an idea of the economic value of cobalt, it is interesting to note that one of the largest mines in Congo (Mutanda) produces about 250 kt/y of Cu and 25 kton/y of Co, but the latter generates about 40% of the revenues.[18] Cobalt refining is also a matter of concern because most of it is done in China. The trade flow of Ni-Co and Cu-Co ores from DRC and other countries to China is a multibillion affair that feeds the Chinese manufacturers of LIB cathodes.[18] This is one of the (many) strategic activities behind the ongoing "trade wars" between China and the USA.

The benefits and concepts related to the reuse and recycling of LIBs discussed for lithium fully applies – and even more strongly so – to the more critical cobalt. Indeed, at present, LIB recycling is much more attractive for cobalt than lithium due to its higher economic and material value. At any rate, the extensive use of LIBs is a relatively recent trend, therefore large-scale recycling can be effectively accomplished not earlier than 2025, with EU possibly obtaining about 10% of its Co supply for the EV sector from end-of-life batteries in 2030.[39]

- *Graphite.* The dominant material for LIBs anodes is graphite, sometimes added with small amounts of silicon oxides. Both synthetic graphites (SGs) and natural graphites (NGs) are normally utilized, with an almost equal market share. NGs tend to be less performing, but they are about 50% cheaper than SGs.[16] NGs occurs in several forms (amorphous, flake and vein) and its quality is dictated by the carbon content and the grain size; battery grade NG must have a very high carbon content (> 99.95%) and particles sizes in the range 10-25 μm for optimal operations.[43] Availability of natural graphite is not a matter of concern in itself because the annual world demand is around 1 Mt and estimated world reserves are currently placed at 300 Mt.[44] New extraction projects are under development in several parts of the world, particularly in Africa (Tanzania, Mozambique), North America and Australia; reserves in Europe appear to be very limited.[43] Presently, the issue with natural graphites is that over 60% are produced in China (the rest primarily in Brazil and India), which makes this anode material the most geographically concentrated component of LIBs in terms of supply, even more than cobalt.[18,45] However, less than 10% of graphite is used for batteries, the primary application being refractories, due to its high temperature stability and chemical inertness, and steel making.[43] The share of graphites used in LIB manufacturing is expected to increase dramatically in the next decade.[45]

- *Dysprosium.* The most widely used motors in electric vehicles are based on permanent magnets (PM) which are made of the neodymium-iron-boron (NdFeB) alloy,[46] primarily in a $Nd_2Fe_{14}B$ tetragonal crystalline structure. At present, NdFeB is the dominant high-performance permanent magnet material due to its superior magnetic flux output per unit volume, which is almost ten times as much compared to ferrite. Besides electric motors, NdFeB is used in several applications such as wind turbines, computer drives and headphones. The NdFeB alloy is made in different variants, with minor concentrations of other rare earths (dysprosium, praseodymium, terbium) or transition metals (copper, cobalt, niobium) capable of optimizing the alloy's properties for specific applications. Dysprosium is used to enhance the performance of NdFeB magnets at high temperatures (up to about 7% in weight), such as those reached inside electric motors.[47] About 90% of BEVs presently sold have permanent magnet motors, whereas induction motors, which do not require rare earth elements (REE), cover most of the rest. PM motors are up to 15% more efficient and the combined weight of metals used in PM motors is also 15% smaller than induction motors, despite the presence of REE. The latter account for a tiny percentage of the overall motor weight, which is mainly dictated by laminated steel and copper.[47]

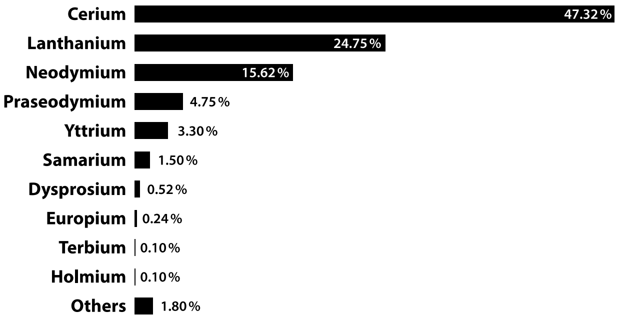

Figure 9. Production of rare earth oxides in 2017.[52]

REE are not rare on the Earth's crust, but they are rarely found at concentrations making extraction viable from the technical and economic point of view. Accordingly, rare earth mines are very few worldwide and prices are highly volatile. Dysprosium makes less than 1% of the global production of rare earth oxides, while neodymium is about 16% and is substantially cheaper (Figure 9).[48,49] This physical and economic constraint has prompted technological improvements leading to a decrease in the use of dysprosium by 50% (from about 120 to 60 g) in the average EV.[47] This allowed a stabilization of the global demand of dysprosium oxide, which is almost completely covered by China. In the years to come, a large expansion of the EV market is expected and, in spite of an enhanced efficiency in the use of dysprosium in permanent magnets, it is expected that its demand will increase to such an extent that China alone will no longer be able to cover it with legal production (illegal mining of REE in China is common).[47]A number of new mining projects of rare earths are under development in several countries, including Australia, Canada, Chile, Namibia and Greenland.[47] Therefore, a relieve on the supply of dysprosium and, more generally, of rare earth elements is expected, also in light of the increasing efforts aiming at recycling REE[41] and replacing the most rare ones in new magnet formulations.[50,51]

EFFICIENCY, ELECTRICITY, CONSUMPTION AND ENVIRONMENTAL IMPACT OF BATTERY ELECTRIC VEHICLES

Level 1 – Tank-to-wheel vs. battery-to-wheel and the overall electricity consumption of BEVs

The average consumption of a modern 150 hp car is around 6 liters of gasoline for 100 km, which corresponds to about 60 kWh in terms of thermal energy content of the fuel. An equally rated electric car (e.g., Nissan Leaf 2018) runs at least 250 km with its fully charged nominal 40 kWh Ni-Mn-Co lithium ion battery (actual: 38 kWh). In a nutshell, the energy consumption of the gasoline car is 0.60 kWh/km, i.e., four times higher than a BEV (0.15 kWh/km). If one considers losses due to battery charging and discharging (5-20%, depending on specific conditions of temperature, current intensity, etc.) a BEV is still over three times more efficient than an ICV of comparable power.

Assuming a yearly mileage of 15,000 km, a medium-size EV (0.15 kWh/km) consumes 2,250 kWh/y, i.e., less than the average EU household (3,500 kWh/y). It has been assessed that if 80% of EU cars were electric by 2050, the EU electricity demand would increase by only about 10%.[53] The desirable scenario of an overall decrease of the number of cars in the EU in the next decades would make electricity demand for personal car transportation nearly insignificant. Let us put these consumption numbers in a specific national context. In Italy there are 37 million cars, running an average 12,000 km/y. If they were all electric – assuming 0.18 kWh/km by including charging/discharging losses – they would require 80 TWh/y of electricity. Italy already produces over 110 TWh/y only by renewable sources (hydro, PV, wind, biomass, geothermal). Therefore, by increasing 70% only renewable electricity production with respect to current levels, all Italian cars could in principle be powered by renewables. The target is very ambitious but not unrealistic in a 20-year time window, particularly in the perspective of a very likely climate crisis that may foster drastic political decisions and, hopefully, bring about a more moderate use of individual transportation. It must be emphasized that a strong expansion of the EV market in the next 20 years would be fully sustainable in terms of electricity demand, but might find bottlenecks regarding the availability of critical materials such as cobalt (see above).

Level 2 – The influence of the electricity production mix on greenhouse gas (GHG) emissions of BEVs

This issue has been examined in many studies, and there is a general consensus that greenhouse gas emissions (primarily CO_2) associated with the use of BEVs are lower compared to ICVs, when the electricity production stage is factored in.[27] In Figure 10 are reported the results of a recent study where GHG emissions of gasoline and diesel cars vs. BEVs are thoroughly analyzed, in relation to the electricity mix of every EU country and taking into account upstream emissions (extraction, transport, refining of fossil fuels) and cross-border electricity trade among different countries.[54]

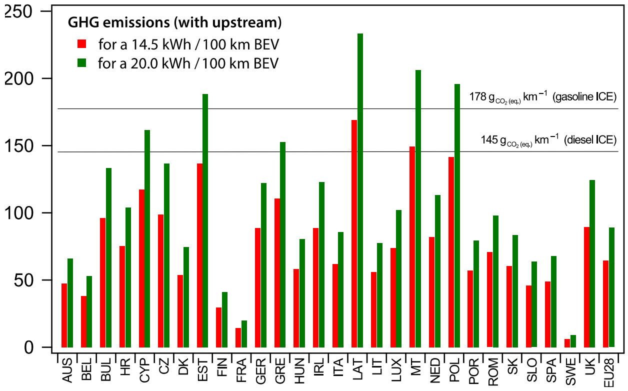

Figure 10. Greenhouse gas (GHG) emissions of electric vehicles in the countries of the European Union vs. gasoline and diesel cars, taking into account the electricity generation mix and cross-border electricity exchange.[54]

Small/Medium-size BEVs (14.5 kWh/ 100 km) entail a lower GHG emissions than gasoline ICVs in every EU country and perform worse vs. diesel only in two countries (Latvia and Malta) in which electricity production is strongly based on coal and oil (Malta is now switching to gas). On the other hand, the GHG emission of BEVs is much lower than ICVs in countries with a strongly decarbonized electricity portfolio such as Sweden, France, Finland, Austria and Denmark, which primarily rely on nuclear, hydro, wind and biomass. It is noteworthy the good performance of BEVs in Italy, a big exporting industrial economy with a renewable electricity production close to 40%.

It must be emphasized that all of these data can be considered a superior limit, as they do not take into account a simple fact. At least in this initial stage, BEV owners are typically more environmentally concerned than the average citizen and often feed their cars with self-produced PV electricity or sign contracts with utilities that sell renewable electricity packages. Such a bargaining power, which of course cannot be exerted at the gasoline pump with ICVs, can speed up the "greening" of the electric system in a bottom-up fashion.

Level 3 – Overall life-cycle assessment of battery electric vehicles

Assessing the environmental impact of BEVs over the entire lifecycle is a complex exercise that depends on several factors, such as the size of the vehicle considered, the electricity production mix, the location of the mineral resources for batteries and whether the comparison is made with diesel or gasoline cars. The European Environment Agency has recently released an excellent report on the state of the art in the field, where details on impacts assessed at the different stages of the industrial chain are reported: raw materials extraction, production, use, end-of-life.[27] The component that makes the biggest difference between BEVs and ICVs is of course the battery. It has been consistently reported that the extraction of battery materials has a substantial impact in terms of human, freshwater and terrestrial ecotoxicity, as well as freshwater eutrophication. In this domain, the comparison with ICVs may be presently unfavourable[55] and the single most important factor leading to this result is the use of electricity produced from fossil fuels in raw materials extraction and battery manufacturing.[27] Besides the use of renewable electricity at every stage of LIB production, use and disposal, other relevant factors that can improve the life-cycle environmental performance of BEVs vs. ICVs are (i) using them for at least 150,000 km and (ii) better transparency of car firms through the implementation of traceability protocols along the whole raw materials supply chain, so as to constantly monitor social and environmental impacts.

Finally, putting the BEV industrial supply chain in the context of circular economy is crucial for the end-of-life management.[27] To this end, legislations around the world must promote as much as possible the implementation of Extended Producer Responsibility (EPR) practices, which make product manufacturers responsible for the entire life-cycle of their products and especially for the take-back, recycling and final disposal. In the last decades, several governance mechanisms have been introduced on waste disposal and mineral recycling processes for electronics and batteries. Recycling practices related to BEVs are already and will continue to be shaped by these national and international regulations, which will become stricter as electric mobility will expand.[56]

The number of BEV to recycle is presently insignificant, but companies and legislators must be ready for the first wave of end-of-life BEVs which will occur in the 2020s.

CONCLUSION

After one century of undisputed dominance of the internal combustion engine, the road transportation sector is slowly undergoing an epochal transformation towards electric powertrains. This trend is dictated by two main factors: the quest for enhancing the energy efficiency of vehicles and the need of improving air quality in urban areas for the sake of public health. Another factor that may foster the market expansion of EVs is the supply and/or price of oil in the long term. At present, oil is cheap and plentiful,[57] but it is increasingly obtained from unconventional resources[58] (e.g., shale rocks, tar sands, conventional wells in extreme environments), which are characterized by stronger carbon footprints, heavy environmental impacts, questionable economic returns, poor energy return on energy invested (EROI).[59] On the other hand, the constant increase of renewable electricity production and the possibility to deploy vehicle fleets which are intrinsically less dissipative (batteries are far easier to recycle than CO_2) can ultimately be a major driver for the transformation of the car sector.

There is debate on which extent electrification will permeate the way of moving persons and goods in the next decades. In our opinion, BEV will be dominant for personal transportation (cars, SUVs, motorbikes, bikes) because the ubiquity of the recharging infrastructure (i.e., the electric grid) is a formidable asset versus potential competitors lacking an energy distribution base (e.g., hydrogen).[60] On the contrary, we believe that battery-based transportation will be far less relevant for trucks and buses, due to the huge material demand this would imply for manufacturing batteries. Since heavy duty vehicles are often collected in large parking lots and run more predictable routes, it is reasonable to expect that they may be preferentially electrified via fuel cells,[61] fed by hydrogen or liquid fuels produced in large centralized facilities. In this regard, it is needless to say that an even more rational solution for freight transport is shifting as much as possible to railways, which are largely existing and often underutilized in several countries.

Lithium ion battery is the key enabling technology for the development of road electric transportation, with a number of different chemistries now available for the cathode, but less practical solutions for the anode, beyond graphite materials. It can be reasonably expected that no practical alternatives to LIBs will be found in the next decade and perhaps even beyond, also because the huge ongoing investments in LIBs manufacturing make it harder for potential alternatives (e.g., lithium-sulphur, lithium-air or sodium/magnesium based batteries)[62] to become economically or technically competitive.[16] Unfortunately, the energy sector is afflicted by frequent claims of "revolutionary" inventions or discoveries, with scientists sometimes too bold in communicating results to the general public, without properly highlighting the limits of their work for commercially viable applications.[63]

The road transportation sector claims about 50% of the world oil supply and emits about 18% of global CO_2 emissions,[64] therefore the electrification of road vehicles is a key milestone of the global energy transition, because almost 30% of the world electricity supply is *already* generated by renewable WWS technologies (Water, Wind, Solar)[65] and will grow further in the years to come, due to massive investments worldwide, with China as leader.[66] However, in order to make this process truly beneficial for society, it is necessary that the global industrial supply chain of LIBs – all the way from raw materials extraction (concentrated in South America, Africa and Oceania) to battery manufacturing (primarily in China, Japan and South Korea) to usage (mainly in North America, Europe, China, Japan) – is made environmentally and economically sustainable.

Regarding physical availability of materials, cobalt represents a real risk, whereas lithium appears to be of lower concern. At any rate, integral recycling of LIBs at the industrial scale is becoming mandatory because it is presently projected that there will be 140 million EVs on the road by 2030 (10-15% of the global share), with 11 million tons of LIBs reaching their end-of-life service throughout the next decade.[67] The biggest obstacle in this direction is the fact that batteries are manufactured in several forms, sizes, and chemistries, hence a variety of disassembly/recycling protocols needs to be established, increasing technical and economic costs. Ultimately, failure in addressing the recycling issue could endanger the expansion itself of the BEV market, as availability of some virgin raw materials (particularly cobalt) could turn out to be an insurmountable physical limit, also in view of the rise of another potentially huge market such as backup battery packs for intermittent renewable technologies.

In principle, electric vehicles might be an integral part of smart electric grids, serving as two-way electricity dispatchers on demand (V2G, i.e., vehicle-to-grid concept)[68] thus helping to shelve peak demand. This approach has several pros and cons, for instance the car owner could make a profit of his/her "mobile storage system", but the lifetime of the battery would be negatively impacted. The rational of this idea is compelling: 97% of their lifetime vehicles are idle. However, an effective implementation of V2G require substantial advancements at the grid and battery level.

Presently, the car battery industry is focusing on three priorities to be fully competitive with traditional thermal cars: a price of 125 $/kWh for LIB packs,[16] higher energy densities (up to 500 Wh/L, pack level)[16] to extend driving ranges beyond 500 km, and the consolidation of fast charging networks. A relevant issue to address is the modernization of the commercial network of car companies, which is unprepared (if not unwilling) to offer electric models to customers.[69]

It must be emphasized that the final objective of the electric revolution should not be the replication of the presently inefficient and unsustainable system heavily based on individual mobility, with an increasing urban population trapped in traffic jams, albeit "electric". The great transition to be possibly accomplished within the next 30 years primarily concerns the development of public, mass, light and smart transportation, which entails buses/metros, railways, bike lanes, shared mobility, autonomous driving. The desirable expansion of the BEV market is only one of the ingredients to achieve a radical change of the transportation system towards new, rational and resource efficient paradigms that make cities designed for people and not for automobiles.

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