Review

Fuels, power and chemical periodicity

B. Yao[1], V. L. Kuznetsov[1], T. Xiao[1], X. Jie[1], S. Gonzalez-Cortes[1], J. R. Dilworth[1], H. A. Al-Megren[2], S. M. Alshihri[2] and P. P. Edwards[1]

[1]KACST-Oxford Centre of Excellence in Petrochemicals, Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK
[2]Materials Division, King Abdulaziz City for Science and Technology, Riyadh 11442, Kingdom of Saudi Arabia

PPE, 0000-0002-1379-9400

The insatiable—and ever-growing—demand of both the developed and the developing countries for power continues to be met largely by the carbonaceous fuels comprising coal, and the hydrocarbons natural gas and liquid petroleum. We review the properties of the chemical elements, overlaid with trends in the periodic table, which can help explain the historical—and present—dominance of hydrocarbons as fuels for power generation. However, the continued use of hydrocarbons as fuel/power sources to meet our economic and social needs is now recognized as a major driver of dangerous global environmental changes, including climate change, acid deposition, urban smog and the release of many toxic materials. This has resulted in an unprecedented interest in and focus on alternative, renewable or sustainable energy sources. A major area of interest to emerge is in hydrogen energy as a sustainable vector for our future energy needs. In that vision, the issue of hydrogen storage is now a key challenge in support of hydrogen-fuelled transportation using fuel cells. The chemistry of hydrogen is itself beautifully diverse through a variety of different types of chemical interactions and bonds forming compounds with most other elements in the periodic table. In terms of their hydrogen storage and production properties, we outline various relationships among hydride compounds and materials of the chemical elements to provide some qualitative and quantitative insights. These encompass thermodynamic and polarizing strength properties to provide such background information.

We provide an overview of the fundamental nature of hydrides particularly in relation to the key operating parameters of hydrogen gravimetric storage density and the desorption/operating temperature at which the requisite amount of hydrogen is released for use in the fuel cell. While we await the global transition to a completely renewable and sustainable future, it is also necessary to seek CO_2 mitigation technologies applied to the use of fossil fuels. We review recent advances in the strategy of using hydrocarbon fossil fuels themselves as compounds for the high capacity storage and production of hydrogen without any CO_2 emissions. Based on these advances, the world may end up with a hydrogen economy completely different from the one it had expected to develop; remarkably, with 'Green hydrogen' being derived directly from the hydrogen-stripping of fossil fuels.

This article is part of the theme issue 'Mendeleev and the periodic table'.

1. Introduction

How the world can provide abundant fuel, power and energy supplies while dramatically reducing CO_2 emissions is one of the defining issues of our time. The challenge is huge but this is a pivotal moment. Rarely have the opportunities for progress been as exciting, yet the challenges so existential. We are convinced that advancing the best technology to confront this grand challenge must—and will—stem from an understanding and advancement of basic scientific principles. Such a generality is as true in the world of fuel and power as in any other technologies. No more so than an understanding and appreciation of how the physico-chemical properties of the chemical elements, and their compounds, lay a solid foundation for such principles. Such a foundation for the periodic table of the elements is provided by the Periodic Law. In its modern expression, the Periodic Law states that *the properties of the chemical elements are a periodic function of the atomic number* [1].

There is much unity in this powerful principle and we will attempt to illustrate its widespread applicability in the field of energy—ranging from an understanding of the pre-eminence of coal and fossil fuels in sustaining our current, complex way of life to the necessary shift from carbon-rich to hydrogen-rich compounds, finally to hydrogen as fuels. In the following sections, we survey aspects of the characteristic properties of the chemical elements, and their compounds which correlate energy production and properties across the periodic table. Catalysis does—and will—play multiple, important roles in all aspects of energy production and storage. However, our emphasis is primarily on thermodynamics and other periodic correlations in properties; these can lay the 'ground rules' for the further application of catalysis.

2. Current sources of energy and power; dominance of the elements carbon and hydrogen

The whole of our world civilization is based upon an unceasing availability of quantities of power supplied by machines. Industrial humankind has primarily and principally derived power from the burning of fuels; that process continues at this point in time—and almost certainly will do for the foreseeable future. While any substances which unite with the evolution of heat must strictly be defined as fuels, the industrially-significant fuels are limited in type.

The function of a fuel is to provide the energy—and with that the power—for a multitude of applications from small, through intermediate to huge scale. For the fuel to have any practical use, it must undergo a highly exothermic reaction with atmospheric air—that is, a chemical element or compound must have a large heat (enthalpy) of combustion—and in that process of aerial combustion, it must release a significant quantity of energy per kilogram of fuel.

The fuels most widely used are invariably commonly available carbonaceous materials which can be easily burned in air producing a copious and easily controlled evolution of heat. The most important fuels are carbon (coal) or hydrocarbon fossil compounds. It is no exaggeration
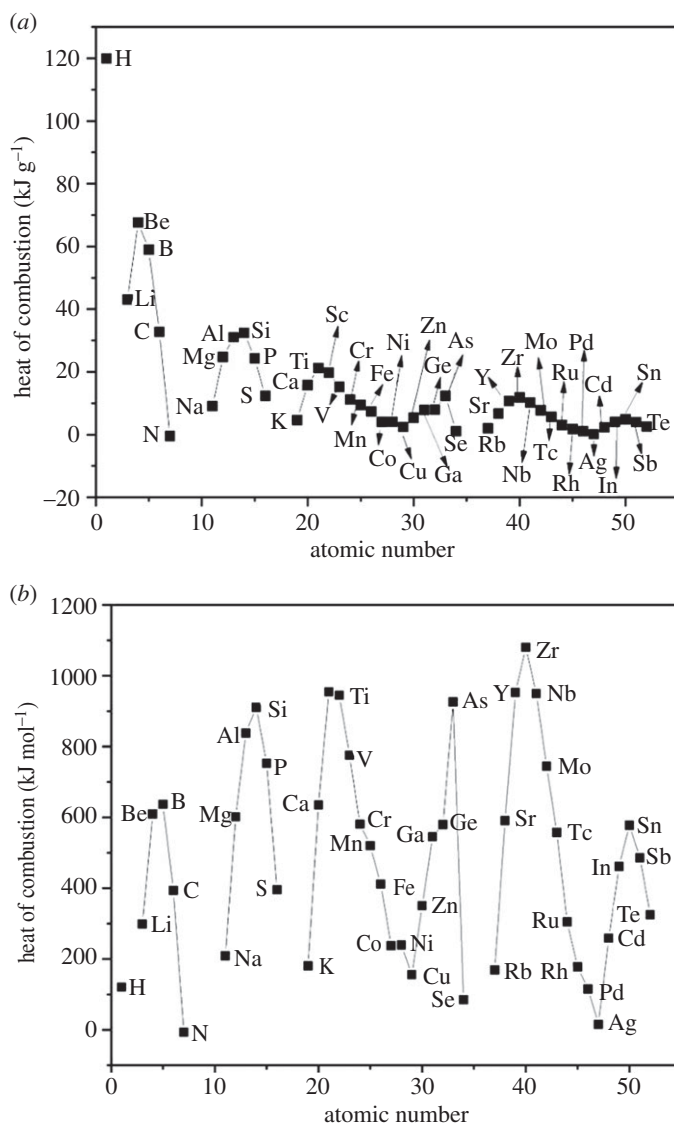
Figure 1. Heat of combustion (*a*) kJ per gram and (*b*) kJ per mol of elements of the periodic table.

to say that the energy which has driven and now drives our whole modern industrial society is sustained primarily through the following two chemical reactions:

$$C + O_2 \rightarrow CO_2 \tag{2.1}$$

and

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2.2}$$

For all their faults—mainly attributed to the chemical combustion reaction (2.1)—carbon and hydrocarbon fossil fuels remain relatively inexpensive, widely available and readily adaptable to applications large and small, simple and complex. The importance of hydrocarbons as fuels, therefore, cannot be overstated.

It is noteworthy that in any such discussion, as the first recourse in looking for the origins of the use of chemical elements as high energy fuels in aerial combustion reactions, one can naturally turn to the periodic table for rationalization. Figure 1 shows the heat of combustion of most of the chemical elements, plotted against their atomic number. As noted by Lothar-Meyer & Mendeleev
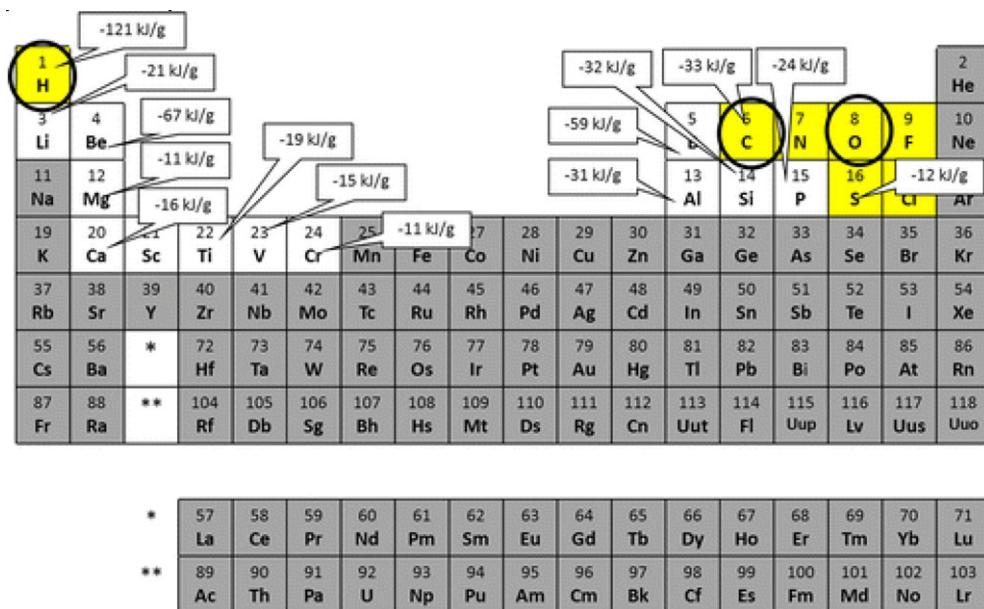
Figure 2. Elements with enthalpy of oxidation (combustion) greater than 10 kJ g^{-1} are labelled with caption boxes. Elements with nonsolid oxides are indicated by yellow boxes. Circles highlight the only three elements left after eliminating elements with: (i) solid oxides as oxidation products, (ii) low heat release upon aerial oxidation and (iii) toxic oxides as oxidation products. Oxygen is included because oxygenates have combustion chemistry advantages in spark-ignited engines and are conveniently derived from biomass. Taken from [3]. Copyright 2013 ACS. (Online version in colour.)

[2], the principle of a periodic function of a chemical element's atomic mass (and now atomic number) applies here, even when one is rationalizing their properties as fuels.

On a purely weight-for-weight basis, liquid hydrogen clearly has the highest heat of combustion of any element; that element—first on the periodic table—therefore represents the ultimate in a fuel. However, its low density and low boiling point introduce significant problems both for handling and storage, challenges which will form a later part of this paper.

For the type of universal applications necessary for humankind over the ages, it is now recognized that a fuel typically needs to liberate at least $10 \, \text{kJ} \, \text{g}^{-1}$ upon aerial combustion. Furthermore, of course, a fuel and its resulting oxidation product should be safe and easy to handle; most notably the combustion product should not be a solid and must not be toxic. Interestingly, these various requirements then impose a natural selection for candidate chemical elements across the periodic table (figure 2). Here, elements with gaseous or nonsolid oxide combustion products are indicated by yellow boxes. Circles highlight the chemical elements remaining after eliminating elements with; (1) solid oxides as their combustion product (2) low heats of oxidation and (3) toxic oxides as their combustion product (e.g. S).

From such an examination, it is abundantly clear why the elements H and C in the form of coal and (fossil) hydrocarbons have been the pivotal chemical elements in the periodic table which have sustained humankind's fuel-for-power for many thousands of years.

The use of fuels involving the combination of the elements hydrogen and carbon (as coal and/or hydrocarbon fossil fuels) as highly effective sources of power has—without question—increased and supported our comfort, longevity, affluence and population size. For example, there is a well-established, strong correlation between *per capita* energy use and key social indicators such as the UN's Human Development Index and that energy use is still dominated by fossil fuels.

Energy and power from fossil hydrocarbon fuels is, however, a double-edged sword. The use of coal and hydrocarbons as fuel/power sources to meet our economic and social needs is now recognized as a major driver of the most dangerous environmental changes, including global climate change, acid deposition, urban smog and the release of many toxic materials. No more so than the ubiquitous aerial combustion product CO_2, now recognized as the main driver of climate change. Such problems are exacerbated by the increase in human population as well as the over-dependence of our society on these hydrocarbon resources.

Significant and recognizable climate changes have now become one of the greatest challenges of the twenty-first century. Turning to potential energy solutions, the chemical element hydrogen has emerged as an alternative, attractive source of energy and power through a future hydrogen energy economy.

3. Future source of clean energy and power; the element hydrogen

Hydrogen as a carrier of energy and power, particularly in association with fuel cells, has long been seen as a bridge from the present Carbon Economy to a sustainable Hydrogen Energy Economy future. There is a growing consensus that ultimately the world's future energy needs will be met by hydrogen and this hydrogen will be used to power fuel cells.

Steam methane reforming (SMR) is currently the main hydrogen production process in industry, but it has high emissions of CO_2, at almost 7 kg CO_2/kg H_2 on average, and is responsible for about 3% of global industrial sector CO_2 emissions. A promising route for hydrogen production is high-temperature pyrolysis (decomposition in the absence of oxygen) of hydrocarbons, biomass and municipal solid waste into hydrogen and (solid) carbon black, accompanied by its industrial use and/or easy sequestration. At present, the cost of this process is higher than that of steam reforming of natural gas. Hydrogen can also be produced by splitting water through various processes, including electrolysis, photo-electrolysis, high-temperature decomposition and photo-biological water splitting. The commercial production of hydrogen by electrolysis of water achieves an efficiency of 70–75%. However, at present, the cost of hydrogen produced by this route is several times higher than that produced from fossil fuels. Renewable sources of energy (e.g. wind, tidal, hydro, biomass) might provide local sources of hydrogen, but certainly will not meet the massive volumes of hydrogen required globally for the new energy source. The use of nuclear energy (both fission and fusion) to supply future needs for hydrogen energy is also under consideration. Solar energy is most likely the only source of energy capable of producing the amount of hydrogen required to supply a hydrogen economy.

A representation of a possible energy future built predominantly around hydrogen and fuel cells is given in figure 3.

As one can see in figure 3, of fundamental importance, apart from the methane steam reforming, hydrogen can be produced from numerous energy sources—whether renewable or of a fossil origin—and fuel cells based on hydrogen (or hydrogen-containing compounds) offer many advantages over other power sources, particularly for transportation needs. Hydrogen fuel cell vehicles do not emit CO_2 or hazardous emissions during operation. However, hydrogen is a secondary energy carrier and is at present mostly produced from carbon-based primary energy sources. Hence, the CO_2 emission in their operation is primarily due to the hydrogen production process.

The generation of hydrogen (ideally from renewable sources) as well as its storage in sufficient quantities are now substantial challenges which will have to be solved to enable any transition to a future, genuinely renewable Hydrogen Energy Economy.

Although hydrogen contains more energy on a weight-for-weight basis than any other element in the periodic table (figure 1), unfortunately, since it is the lightest chemical element it also has a very low energy density per unit volume.

One of the crucial technological barriers to the widespread use of hydrogen as an effective energy carrier continues to be the lack of a safe, low-weight and low-cost method of storing
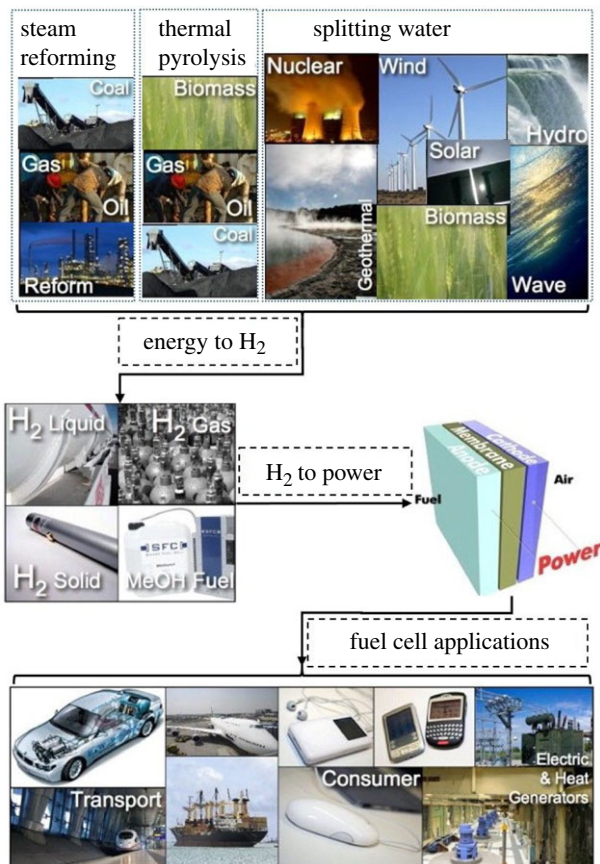
Figure 3. Hydrogen and fuel cells: a representation of a sustainable energy future. Here, hydrogen as an energy carrier links multiple sources and production methods to various fuel cell applications. Modified from [4]. (Online version in colour.)

hydrogen with a high-enough energy density. This has been—and many would argue still is—one of the main obstacles to the widespread adoption of hydrogen as a future fuel, energy and power source.

In principle, hydrogen can be stored either in its elemental form, as a gas or liquid, or in a chemical form. Nowadays, the storage of elemental H_2 is feasible (and indeed practised globally) by several physical methods, such as storage as a gas under high pressure or as liquid hydrogen at cryogenic temperatures. Even though these solely physical storage systems are currently widely adopted, they still comprise many technical and 'social' issues.

The storage of hydrogen in either its solid or liquid compounds has always been seen as an attractive alternative, particularly with respect to the necessarily high gravimetric and volumetric densities required for applications in vehicles with fuel cells that use proton-exchange membrane (PEM's) technologies. Here, we concentrate primarily on the storage of hydrogen in its compounds of the periodic table for such applications. We discuss the properties of these storage compounds in term of periodic trends, particularly in relation to the key operating parameters of hydrogen gravimetric storage density and the desorption/operating temperature at which the requisite amount of hydrogen is released for use in the fuel cell.

An overview or sorting map of the key storage characteristics of a variety of compounds of hydrogen is shown in figure 4 [5] in which we plot the thermal decomposition/release temperature, T_{dec}, (under 1 bar H_2 pressure) of hydrogen compounds and materials as a function of their gravimetric weight % hydrogen content (density). The US Department of Energy (DoE) recommended ultimate targets for both parameters is shown as the shaded band.
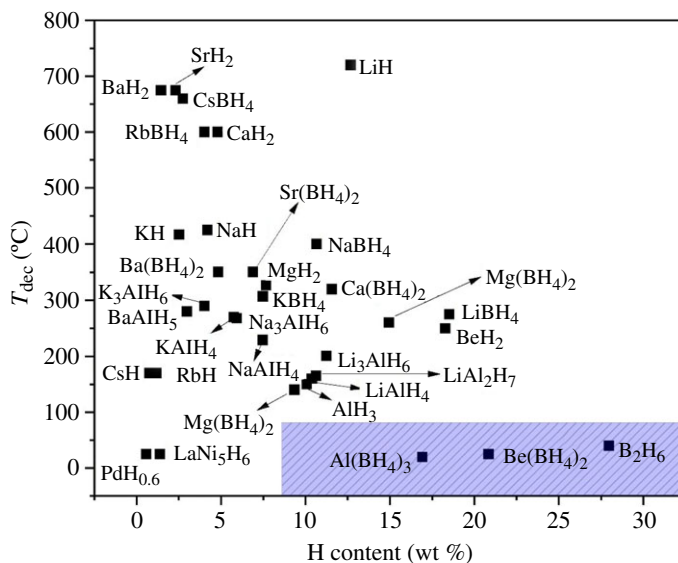
Figure 4. Relation of the thermal decomposition (hydrogen release) temperatures, T_{dec}, and the gravimetric hydrogen content for variety of compounds of hydrogen. The US DoE target ranges for both properties are indicated in the shaded box. Modified from [5]. (Online version in colour.)

The DoE ultimate (accepted) targets are a lower limit gravimetric density/capacity of 7.5 weight % and min/max operating temperatures between −40 and +85°C. [6,7] The hydride compounds and materials shown in figure 4 comprise binary metal hydrides, chemically decomposable hydrides, and complex metal hydrides. The chemically decomposable hydrides have the merits of ambient temperature H_2 generation (such as a rapid chemical reaction with water) but have severe limitations in terms of their regeneration.

By contrast, several binary and complex hydrides contain a high weight % density of H_2 and some exhibit good reversibility (e.g. MgH_2) but they encounter issues with unfavourable thermodynamics and kinetics (the latter in their recycling process following hydrogen desorption). We will concentrate principally on the chemical aspects/chemical control of the basic thermodynamic properties of such compounds and how this relates to identifiable trends across, and down the periodic table. (Extensive reviews which discuss the control of the kinetics of hydrogen absorption and desorption of such compounds are available elsewhere [7–16].)

(a) Binary compounds of hydrogen: the charge on combined hydrogen and its effect on physical properties

Hydrogen combines with the overwhelming majority of elements across the periodic table to form binary hydrides, MH_x. The physico-chemical property of any binary hydride is related to the precise condition of its combined hydrogen, and in particular, the charge on that hydrogen. The range of partial charges on hydrogen in the most representative hydride compounds is shown in figure 5. This parameter, representing as it does a measure of the degree of charge transfer from the hydrogen to the counter element M in each case, serves as a most useful guide in rationalizing the physico-chemical nature of binary hydrides and their periodic trends. When hydrogen bears a partial negative charge, even though this electron excess may be very small, the electrons appear to be available for partial utilization by another atom. This other atom must bear an appreciable positive charge and also have an empty low-energy orbital available.

The physical properties of binary hydrogen compounds vary over a wide range—some are low melting points gases and some are high melting points solids but, as one can see, all these
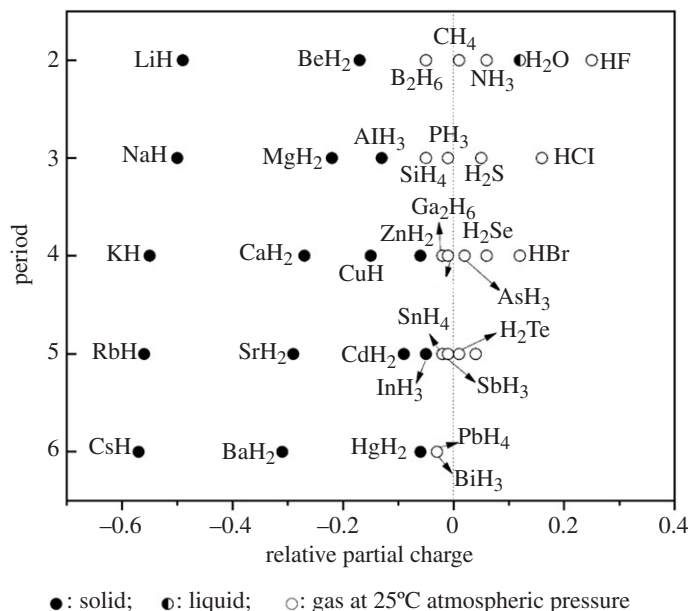
Figure 5. Relative partial charges on hydrogen of binary hydrides, MH_x, of certain chemical elements of the periodic table.

properties are closely related to the relative partial charge on hydrogen. If it is high and negative, the compounds are salt-like solids with ionic crystal lattices (that is, those hydrides to the far left of the demarcation line in figure 5), if it is medium negative, the compounds tend to be solids held together by hydride bridges and if it is low, either positive or negative (close to the demarcation line in figure 5), the compounds are gases (except water, H_2O, as liquid) and the hydride properties are largely determined by its (isolated) molecular structure.

This classification is powerful as it roughly reflects the unique position and nature of the element M in the periodic table [17]. The hydrides of the most electropositive metals are treated as solid ionic compounds with cations M^{n+} and hydride ions approximating to the description H^-; the hydrides of the most electronegative non-metals are best treated (in the extreme) as ionic molecules, containing anions M^{n-} and protons H^+. On the other hand, bonding in the hydrides of elements such as B, C, Si, P, As, etc. is significantly covalent, the coordination environment of the central atom is satisfactorily saturated, and the hydrides of these elements are typically molecular in nature. Finally, many transition metals known to form binary hydrides do so by incorporating H atoms into suitable interstices in what are essentially metallic lattices [18]. We will not discuss these compounds/materials further as their properties are extensively covered elsewhere.

A plot of the gravimetric hydrogen density of binary hydrides versus atomic number of the comprising element is given in figure 6.

The shaded region denotes the US DoE acceptable range, beginning at a minimum of 7.5+ weight %.

It becomes immediately clear that only the light element binary hydrides, having $z < 20$ even come close to the US DoE target of $7.5 +$ wt %. MgH_2, in effect, presents the 'threshold' gravimetric weight % for binary hydrides which may be considered as potential hydrogen storage materials on the basis of that parameter alone. The other key parameter is of course T_{dec}.

The strong chemical bonds that form between hydrogen and certain elements during chemisorption explain the high storage capacity of certain hydrides and their stability at room temperature. However, these strong bonds of course also lead to an enormous energy release during the hydriding reaction. To release hydrogen, the hydride, correspondingly, must be heated to high temperatures in order to supply the sufficient energy to break those same chemical bonds for hydrogen release. Ideal compounds and materials for the storage and desorption of
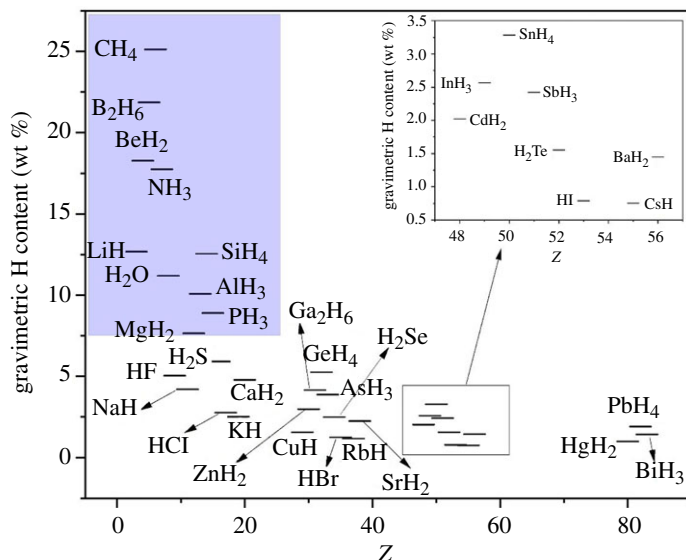
Figure 6. Gravimetric hydrogen content (weight %) of hydrides of the periodic table versus atomic number.
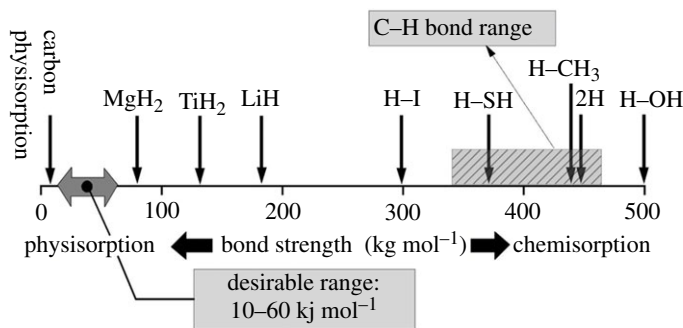

Figure 7. Bond strengths for various hydride compounds of the periodic table. The desirable or targeted range of bond strengths are indicated that allow hydrogen release around room temperature. Physisorption bonding is usually too weak (less than 10 kJ mol^{-1}) and demands cryogenic temperatures for significant hydrogen storage capacity. Chemisorption shows a high stability (greater than 50 kJ mol^{-1}) and demands high desorption temperatures. The ideal binding energy is in the range 10–60 kJ mol^{-1}. A strategy to reduce the chemisorption thermodynamic binding energy (destabilizing) or increasing the physisorption binding energy is generally adopted; we concentrate on the former. Modified from reference [5] with the shaded band reflecting the range of C–H bond strengths for typical hydrocarbon fuels.

hydrogen must, therefore, achieve a compromise between the extremes of physisorption (ideal for reversible sorption/desorption) and chemisorption (ideal for high hydrogen densities). In figure 7, we show the range of binding energies targeted by the US DoE with ideal binding energies for hydrogen within the range of 10–60 kJ mol^{-1} H$_2$; this range nicely sets the limits where the binding energy is strong enough to hold hydrogen but weak enough to allow for the rapid desorption at elevated—but easily accessible—temperatures.

In simple terms, the formation (hydrogen uptake) and the decomposition (hydrogen release) of a binary metal hydride can be represented by equation (3.1) below:

$$M(s) + H_2(g) \rightleftarrows MH_2(s) + \Delta H^0 \tag{3.1}$$
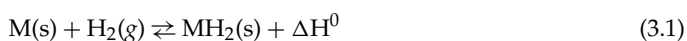
where M is a metal and ΔH^0 is the standard enthalpy of formation of the metal hydride, MH$_2$.
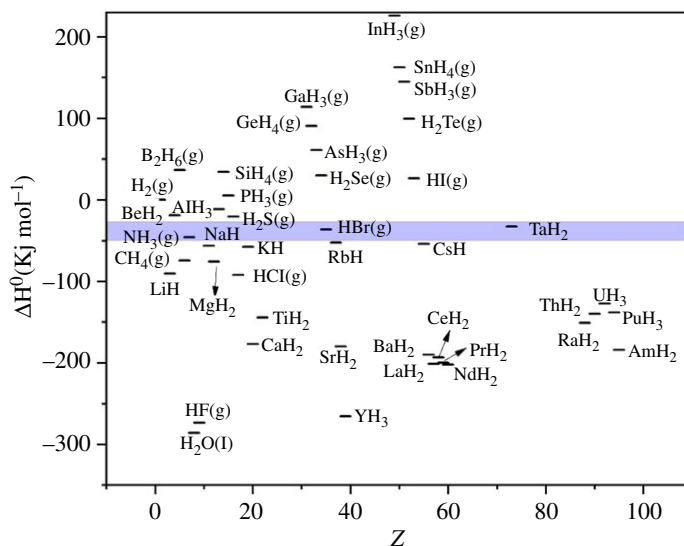
Figure 8. Enthalpy of formation of binary hydrides of elements of the periodic table as a function of atomic number.

The thermodynamic stability of a metal hydride at room temperature requires $\Delta G^0 < 0$, where $\Delta G^0 = \Delta H^0 - T\Delta S^0$, ΔH^0 is the enthalpy change in equation (3.1) and the larger the absolute value of ΔG^0, the higher the thermal stability.

Reading from right to left in equation (3.1) therefore relates to the thermal decomposition of the hydride and its consequent temperature of release of hydrogen for use in applications.

The decomposition or release temperature T_{dec} of a pure metal hydride (at equilibrium pressure) is given by equation (3.2) below:

$$T_{dec} = \frac{\Delta H^0}{\Delta S^0} \tag{3.2}$$

where ΔS^0 is the standard entropy change involved in the formation of the metal hydride.

As a recognized simplification, we take ΔS^0 as the entropy content of gas phase of evolved hydrogen (ignoring, reasonably, the entropy change in the solid hydride).

Therefore, equation (3.2) shows that T_{dec} is expected to be approximately proportional to ΔH^0. Inserting accepted values of ΔS^0 into equation (3.2) leads to a range of ΔH^0 values from about 27 to 50 kJ mol^{-1} and corresponding decomposition temperatures in the range *ca* 25°C to around 130°C, effectively spanning, but nevertheless to the high-end of, the required US DoE operating/hydrogen release temperatures for hydrogen storage materials for use in automobiles.

In figure 8, we show the variation of ΔH^0 with atomic number for binary hydrides of the periodic table and the targeted band of standard enthalpies that allow hydrogen release close to the recognized US DoE target temperature ranges.

In figure 9, we plotted the enthalpy of formation versus T_{dec} for various binary hydrides.

It can be seen from figure 9, as expected, highly stable metal hydrides (i.e. negative enthalpies of formation, ΔH^0) show correspondingly high T_{dec}. The linear relationship also supports the approach usually taken of neglecting any significant entropy changes in the solid hydride.

(b) The complex hydrides: thermodynamic tuning

As in the case of the binary hydrides, hydrogen bearing a substantial negative charge in the complex hydrides of the periodic table can act as an electron donor towards a counter cation if there exists an unoccupied, accessible low-energy orbital. It has been found that complex hydrides
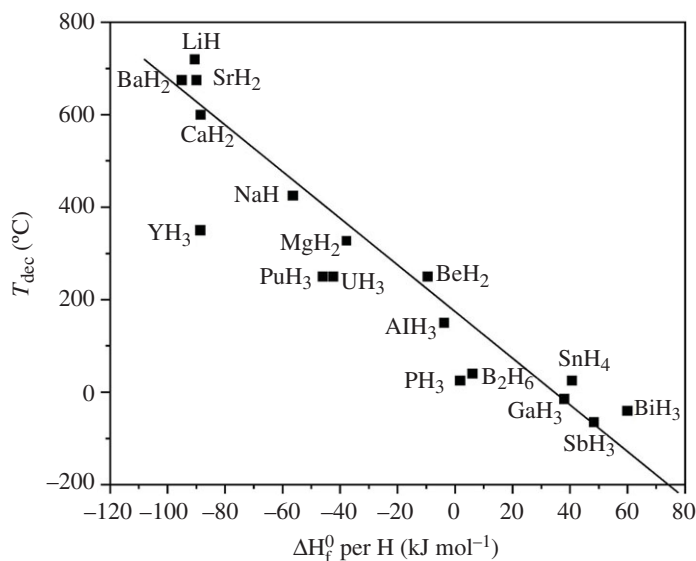
Figure 9. T_{dec} versus the enthalpy of formation for various binary hydrides of the periodic table. Modified from reference [17].

e.g. of boron, aluminium and gallium can be represented in the following manner:

$$BH_3 + H^- \rightarrow BH_4^- \tag{3.3}$$

$$AlH_3 + H^- \rightarrow AlH_4^- \tag{3.4}$$

and
$$GaH_3 + H^- \rightarrow GaH_4^- \tag{3.5}$$

As with the binary hydrides, the thermal stability of complex hydrides of the periodic table varies critically with the nature of the counter cation. In general, the larger the cation, the more stable is the salt and the higher the decomposition temperature.

It is clearly a demanding situation to quantitatively rationalize the observed decomposition trends. For the hydrogen release temperatures of the complex hydrides, some headway is possible if one assumes that the condition of the anion itself is a major factor in determining the stability (and hence T_{dec}). The negatively charged anions in the complex hydrides have relativity expanded electronic/charge clouds that are polarized with (relative) ease by the counter cation. The differences in thermal stability then arise through the extent of the polarization of the anion by the companion cation; the greater that polarization, the less (thermally) stable is the anion itself.

The condition of the anion is, therefore, highly sensitive to the extent to which the complex anion can control its (bonding) electrons, taking into account: (1) the electronegativity of the counter cation, and; (2) the polarizing power of those cations. Thus, as argued elsewhere for the complex oxides of the periodic table [19,20], a rationalization of the relative stability of complex hydrides can arise from considerations of electronegativities, cation radii and polarization effects.

One, therefore, expects that the (thermal) stability of a complex hydride to be greater: (1) the less electronegative the metal and; (2) the larger the metal radius. The anionic part of the complex hydride would accordingly: (1) have greater control of their valence electrons and hence electrical symmetry and stability and; (2) be less distorted by the polarizing power of the cation of the complex hydride. Both factors will lead to higher thermal stability.

In other words, the thermal stability (reflected in T_{dec}) should be directly proportional to the radius of the metal cation and inversely proportional to its electronegativity.

In figure 10, we show how T_{dec} varies with $(r/S)^{1/2}$ for a variety of complex hydrides, where r is the Goldschmidt empirical crystal radius and S is the electronegativity of the atom.
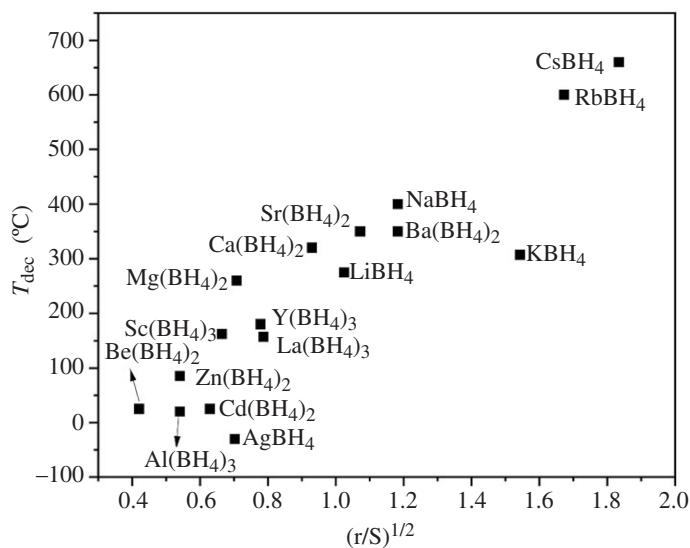
Figure 10. Relationship between the metal radius and electronegativity (through (r/S) ½) to the observed decomposition temperatures of various borohydrides of the periodic table.

Table 1. Polarizing strength, $|Z|/r^2$ [21].

Li$^+$	1.7	Be^{2+}	16				
Na$^+$	1.0	Mg^{2+}	3.3	Al^{3+}	9.2	Si^{4+}	26
K$^+$	0.6	Ca^{2+}	1.8	Sc^{3+}	4.4	Ti^{4+}	9.8
Rb$^+$	0.5	Sr^{2+}	1.2	Y^{3+}	2.7	Zr^{4+}	5.3
Cs$^+$	0.4	Ba^{2+}	1.0	La^{3+}	2.0	Ce^{4+}	3.8
						Th^{4+}	3.3

For the polarizing strengths of cations with inert gas structures, Grinberg assigned the values in table 1 [21]. They are based on a simple electrostatic model, assuming the force on a test charge at the surface of the ion is proportional to $|Z|/r^2$, or the absolute charge over the square of the ionic radius. For these cations, this provides a partial explanation of the often-mentioned diagonal relationship in the periodic table. They also provide a ready rationalization of the polarizing strength of the cation in affecting the anion charge distribution in the complex halides and hence the decomposition temperatures for the production of hydrogen.

This approach helps significantly towards our understanding of the periodicity of the properties of complex hydrides in terms of their hydrogen storage and thermal decomposition properties.

In summary, salts of these complex anions tend to be the most stable (the highest T_{dec}) when the cations are large and of low charge. The higher the charge, and the smaller the cation, the greater its polarizing power on the anion charge cloud. Thus the alkali metal borohydrides, which are presumed to be the most ionic of the family of complex borohydrides, are the most stable and of these the stability increases with increasing size—and therefore decreasing deforming power (polarizing effect)—of the cation.

4. Magnesium hydride: attempts to control and utilise 'The perfect store'

For an optimum hydrogen store, an ideal compound or material should possess: (1) high storage capacity (greater than 6.5 weight % abundance of hydrogen available from the material); (2) low desorption temperature of less than 150°C; (3) high kinetics for hydrogen absorption/desorption; (4) low cost; (5) high abundance; (6) non-toxicity and (7) safe operation (which means a reasonable chemical stability against reaction with accidentally admitted oxygen and/or water) [18]

Remarkably, after many decades of intense study and research expenditure, Mg and its hydride MgH_2 remain the one system across the periodic table that fulfils many of these natural targets. Up to 2019, MgH_2 (and variants) also owns the largest share of publications on solid-state materials for hydrogen storage [22]. Why is MgH_2 still so very attractive in this regard? MgH_2 has the highest reversible storage capacity of all low-z reversible hydrides applicable for hydrogen storage. The hydrides LiH and AlH_3 have higher hydrogen contents 2.6% and 10.0%, respectively, but are simply not suited for hydrogen energy stores since their thermodynamic stabilities are too high, and too low, respectively. Indeed, the storage density/unit volume of MgH_2 exceeds that of liquid hydrogen! Further principle advantages of MgH_2 as a hydrogen storage material are the low costs of the parent Mg metal, its wide distribution in nature, its environmental compatibility and the attractive link in its manufacture to renewable (hydroelectric) energy production.

Important breakthroughs to enhance (3), the hydrogen sorption kinetics of MgH_2, through ball milling to produce nanocrystalline materials and advances in catalytic additives have occurred, and these are extensively reviewed in [9,22–26]) However, the major, fundamental drawback for MgH_2 is its high desorption temperature of well over 300°C (figure 4). As we saw earlier, this is expressed through the high enthalpy of hydride formation.

An interesting approach to improve the dehydrogenation thermodynamics (i.e. reducing the decomposition enthalpy and with that the decomposition or release temperature) involves introducing a new chemical species that reacts with the metal to form an intermediate state. This so-called thermodynamic destabilization lowers the binding energy chemically by incorporating a new element or compound that forms an intermediate state (or states) that reduce the stability of the hydride relative to the non-hydrided state and with that a reduction in T_{dec}.

A classic example is Mg alloying with Si, as shown in figure 11*b*.

$$2MgH_2 + Si \; \rightleftarrows \; Mg_2Si + 2H_2 \tag{4.1}$$

Upon hydrogen release, Mg will not return to its original state but instead form an intermediate compound with a reduction in enthalpy of roughly $40\,kJmol^{-1}$. Thus the hydrogenated state is destabilized or the dehydrogenated state is stabilized. In both cases, this strategy is referred to as destabilization.

Since storage capacity remains a key priority, it is important to achieve destabilization while attempting to minimize the storage capacity reduction through the presence of added elements in destabilized hydrides.

This obvious drawback is clearly evident in the specific case of MgH_2/Si where a reduction in gravimetric density of MgH_2 occurs from 7.6% to 5.0% while, of course, reducing T_{dec}.

In all cases, therefore, there is a tantalizing trade-off between the necessary hydrogen storage capacity and the reduction in the enthalpy of formation and corresponding hydrogen release temperature.

The use of reactive additives to thermodynamically destabilize light element hydride systems has emerged as a powerful and versatile approach for achieving a hydrogen storage material with the required equilibrium properties for potential applications.

Nevertheless, it still remains that fundamental innovations in hydrogen storage technology are needed. Some years ago Sandrock *et al.* [28] noted that to meet the US DoE targets (when considering the hydride container and heat exchange components) one requires a hydride with +7.5 wt.% H_2 capability and relatively low-temperature thermodynamics such that one can use the less than 100°C waste heat of the vehicle fuel cell to provide the heat of H_2 desorption.
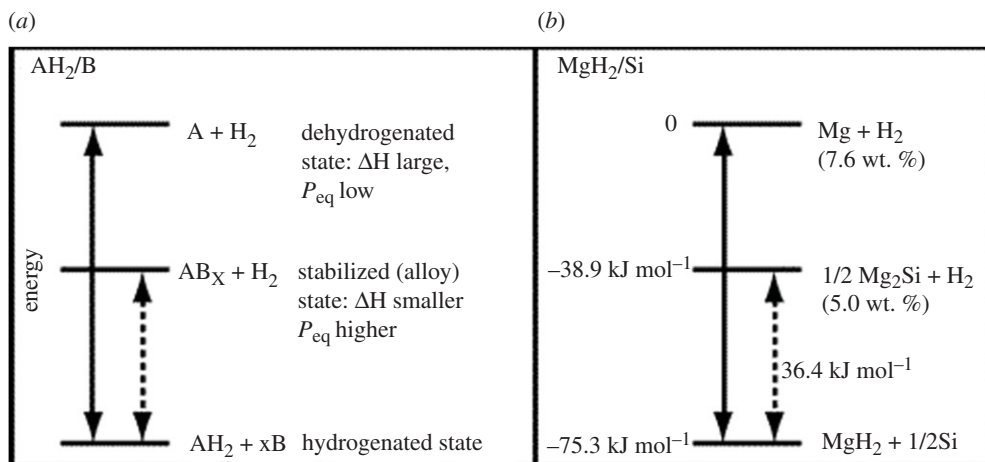
Figure 11. Energy diagrams illustrating hydride destabilization through alloy formation upon dehydrogenation. (*a*) Generic case for a binary hydride (AH_2) with an alloying element (B). (*b*) Example of MgH_2/Si. Alloy formation stabilizes the dehydrogenated state. The hydrogenated state enthalpy does not change. Thus, the enthalpy for dehydrogenation of the pure hydride (solid arrows) is reduced (dotted arrows). For MgH_2/Si, the stability of Mg_2Si reduces the standard enthalpy from zero (pure $Mg + H_2$) to $-38.9\,kJ\,mol^{-1}$ ($1/2\,Mg_2Si + H_2$), and thereby, the dehydrogenation enthalpy is reduced from 75.3 to $36.4\,kJ\,mol^{-1}$. Inclusion of Si also reduces the capacity from 7.6 to 5.0 wt % hydrogen. Taken from [27].

They note *This is far beyond the present state of the art for all known reversible metal hydrides and presents a very strong challenge for us.*

It is our view that this situation for metal hydrides still exists today.

A further telling conclusion from the authors is 'We need new "breakthrough" concepts'.

One such concept and new innovation for the development of hydrogen storage materials is given in the following section where one takes advantage of the intrinsically high volumetric and gravimetric hydrogen densities of fossil fuel hydrocarbons themselves through a new process for the 'stripping' of hydrogen, through microwave-initiated catalytic dehydrogenation.

5. Hydrogen from fossil fuel stores without CO_2 emission

A major barrier to the realization of a Hydrogen Energy Economy still, therefore, exists in the storage and the production of low-carbon hydrogen, and at scale. The accepted and well-established industrial process for the large scale production of hydrogen uses hydrocarbon fossil fuels and water through the steam reforming of methane (SRM) resulting from the endothermic thermal reaction:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \ \Delta H^0 = +163\,kJ\,mol^{-1} \tag{5.1}$$
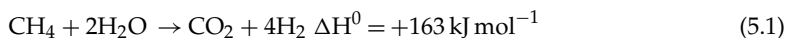
Importantly, it is the use of water (steam) as a reagent in the reaction with fossil fuel hydrocarbons which leads to the formation of carbon oxides. Accordingly, large volumes of CO_2 are emitted into the atmosphere. Note also, it requires quantities of water.

The way out of the situation dating back to the landmark studies of Steinberg [29–31] and also Muradov [32,33] is to adopt the strategy of using fossil fuels for the production of hydrogen *but* to completely change the tactics.

Thus, if the source of hydrogen is *solely the hydrocarbon itself*, we can employ the thermal decomposition process

$$C_nH_m \rightarrow nC + \frac{m}{2}H_2 \tag{5.2}$$

Importantly, from the viewpoint of thermodynamics, this change will not lead to a significant loss. For example, in the case of methane, steam conversion is actually twice as endothermic as
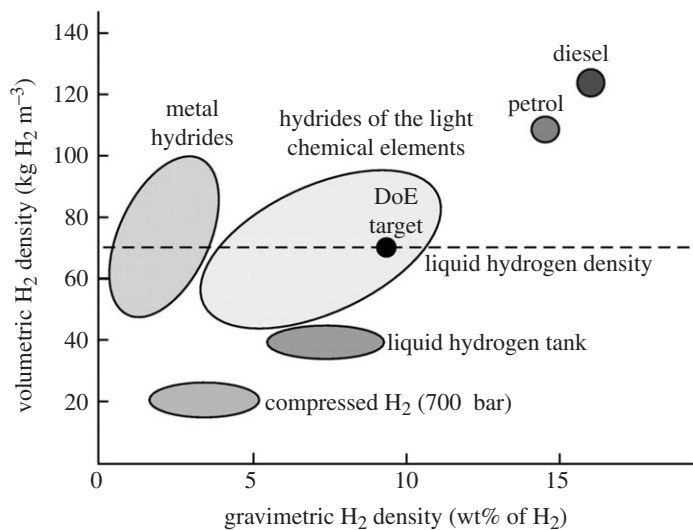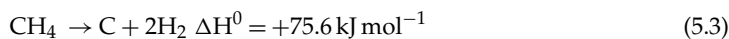
Figure 12. Gravimetric and volumetric densities of various hydrogen storage options (note: weight and volume of the storage container are included). The 'DoE target' represents the US Department of Energy target for 2015 set for an 'ideal' hydrogen storage material. Metal hydrides are conventional, heavy metal hydrides such as LaNi$_5$, etc. Taken from reference [34].

thermal decomposition (per unit volume of methane).

$$CH_4 \rightarrow C + 2H_2 \ \Delta H^0 = +75.6 \, kJ \, mol^{-1} \tag{5.3}$$

Both the attractions of this approach, in terms of high gravimetric and volumetric hydrogen densities of two hydrocarbon fuels, and the challenges, in terms of the high C–H bond strengths that require breaking for hydrogen release, are highlighted in figure 12 (Gravimetric % storage) [34] and earlier in figure 7 (C–H bond strengths).

It is clear that gasoline and diesel hydrocarbon fuels easily exceed the US DoE target for both parametric hydrogen storage densities.

However, with bond C–H strengths for typical hydrocarbon fuels to allow hydrogen release being in the range *ca* 350–500 kJ mol^{-1}, the realization of thermal decomposition *at comparatively low temperatures* clearly requires the innovative use of catalysts.

Recently, the microwave-initiated catalytic dehydrogenation of wax, petroleum and other fossil hydrocarbon fuels have led to major advances in the facile production of hydrogen using inexpensive and abundant fine iron catalysts [35–38].

A plot of the time-dependent hydrogen production from a range of carbonaceous fuels ranging from crude oil itself through to petrol and diesel is shown in figure 13.

For simplification (and recognizing the different chemical compositions of the various hydrocarbons), comparable weight % loading on the same support are given. It is quite clear that at the microwave initiated iron catalysts, a considerable volume of high purity hydrogen was readily produced from the petroleum and heavy liquid feedstocks, and that typically occurs in periods of about 3 min for the production.

The co-product of a dehydrogenation process for a hydrocarbon fuel, solid carbon, will therefore permanently eliminate direct CO$_2$ emissions.

Microwave-initiated catalytic dehydrogenation of fossil fuels could become potentially viable for fuel cell vehicles because of three attractive features: (1) rapid production of high-purity hydrogen (this provided the possibility to produce hydrogen *in situ* for the use in fuel cells, we do not need a high-pressure tank on board for hydrogen storage, but only a tank for petrol/diesel); (2) necessity for only a small-scale microwave source and reactor system easily attainable for modern high power, small microwave devices for either localized or distributed distribution;
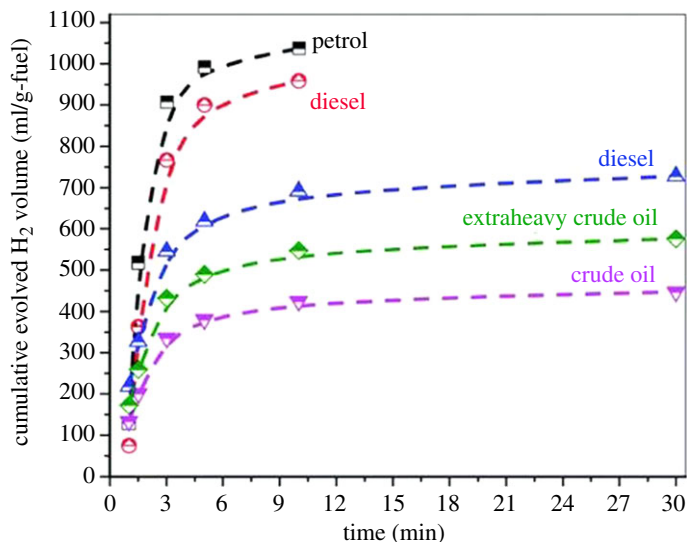
Figure 13. Hydrogen production through the microwave-initiated iron catalysed dehydrogenation of fossil fuels. Taken from [35]. (Online version in colour.)
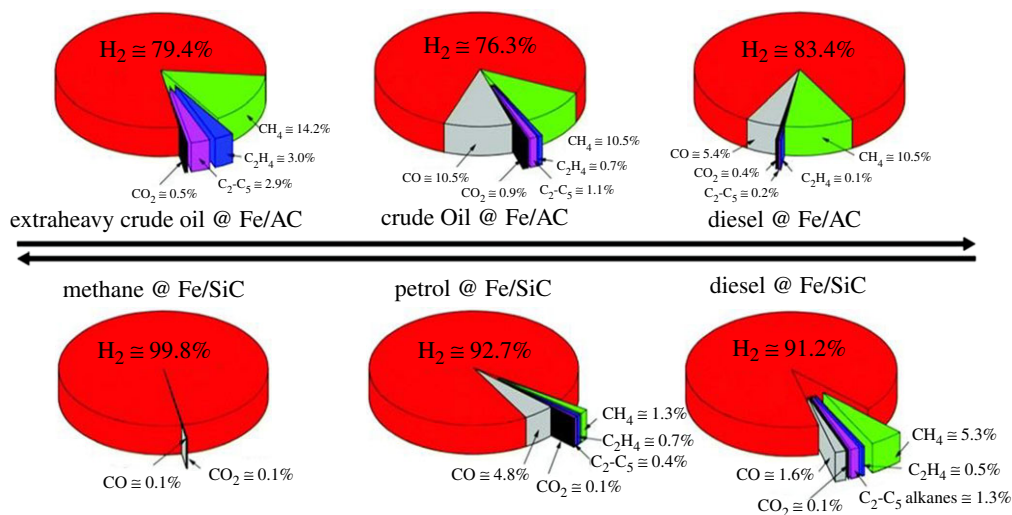

Figure 14. Hydrogen production through the microwave-initiated iron catalysed dehydrogenation of fossil fuels. The evolved gas composition of various fossil fuel feedstocks and products over iron catalysts on silicon carbide and activated carbon following microwave-initiated catalytic dehydrogenation (hydrogen stripping) of the fossil fuels. Taken from [35]. (Online version in colour.)

and (3) well-established distribution infrastructure for fossil fuels. Clearly, further studies are needed in both engineering aspects and the optimization of the entire catalytic process for future applications. Nevertheless, microwave-initiated catalytic dehydrogenation (hydrogen-stripping) of fossil fuels highlights the possible advantages of microwave in the instant generation of high purity hydrogen not only from untreated crude oil but also from a variety of fossil-derived liquid fuels (shown in figure 14).

Of course, one challenge—recognized many decades ago—is what to do with the large quantities of carbon by-product.

However, this challenge is more attractive from both a technological and an ecological point of view to store solid carbon rather than gaseous CO_2. Even larger amounts of gaseous CO_2 emissions have to be sequestered from the corresponding aerial combustion of fossil fuels and with that the ecological uncertainties—and socio-political problems—of storing such large quantities of CO_2. Furthermore, the solid carbon formed could either be stored or sequestered or kept for future use, to then be converted back to high-value chemicals, partly recovering the chemical energy stored in the solid.

The catalytic decomposition of methane to produce CO_2-free hydrogen and solid carbon instead of steam reforming of methane also attracted many researchers. A range of catalysts including Ni-based, Fe-based, noble metal and carbonaceous catalysts have been thoroughly studied. [39–41] Research effort has been recently focused on Fe-based catalysts due to their high efficiency, non-toxicity, low cost, abundance and stability at high temperatures. From figure 14, it can be seen that the microwave-initiated iron catalysed decomposition of methane produces 99.8% purity hydrogen. The high purity of hydrogen indicates that the process has potential application for the production of hydrogen for the direct use in fuel cells. The production of solid carbon and gaseous hydrogen from methane decomposition using a plasma process is being commercially developed in the US. [42]

It has been suggested that in the future, carbon-free hydrogen, perhaps generated from water—with renewable power provided by the sun—will be a major non-polluting energy carrier; thereby labelled as 'Green hydrogen'. The issue is of course that most of the countries with abundant sources of solar energy do not have abundant sources of water! And the idea of using solar energy to desalinate water only then to use it as a fuel surely goes against common experience and current thoughts. In addition, despite enormous efforts worldwide, the solar photodecomposition of water has many technical hurdles remaining.

These recent advances, therefore, suggest another intriguing possibility; namely, the production of Green hydrogen directly from the hydrogen—stripping of hydrocarbon fossil reserves with renewable power provided by the sun. This would be a sustainable, non-traumatic route to the widespread use of hydrogen as an energy source. In this scenario, hydrogen would be produced at or near oil fields through renewable solar energy and piped or transported to centres of use. At the same time, elemental carbon, co-produced with the hydrogen—as a solid or possibly in an emulsion formulation—could be piped to sequestering locations; ideally, these would be at the oil field itself.

Significant challenges still await in these new ideas and these routes are far from widespread practical application, but they are worthy of further investigation and development.

Thus one could enter a new era of decarbonization technologies to mitigate global warming, remarkably, through the use of carbonaceous fossil fuels to produce carbon-free hydrogen. Thus, the world may end up with a hydrogen economy completely different from the one most had expected to develop. If renewable energy could be used for this catalytic stripping of hydrogen from fossil fuels, one enters the era of *Green energy from fossil fuels*!

6. Concluding remarks

The purpose of this article was to outline and rationalize the relationship among the chemical elements and their compounds in their use—and potential use—in the production and storage of energy.

We have focussed on the key energy requirements for fuels (and with that power), overlaying those with the evident chemical and physical trends across the periodic table.

Thus, we have attempted to identify several of these key relationships among the chemical elements and compounds—relationships that show an encouraging degree of rationalization—and periodic order.

Such an approach, for example, helps explain the clear historical—and present—dominance of carbon and hydrocarbon fossil fuels being easily burned in atmospheric air with a copious, easily controlled evolution of heat.

The objective of a fuel is to provide heat and power. However, putting on one side the now-recognized huge impact of CO_2 emissions on our planet, we note the visionary remark made by Macrae in his seminal work . . . .

> It is a sobering thought that all the world-wide, furious activity of prospectors, miners, petroleum engineers, scientists and chemical engineers in the coal and petroleum industries has its fulfilment in the destruction of their products by combustion-fire-conflagration! [43]

It is often stated that our challenge is now to transform our fossil fuel-based energy system into a sustainable or renewable energy system. For that vision, hydrogen is emerging as a most promising candidate energy carrier to provide carbon- and emission-free energy.

We have focussed on the burgeoning challenge of the need for a cheap, safe (non-hazardous, non-toxic) and easily producible hydrogen storage material, again drawing on chemical and physical properties with respect to trends evident in the periodic table.

We highlight that a new scientific and technological era of '*Fossil fuel decarbonization* 'can now beckon. In this, we will not burn fossil fuels for energy and power, but rather use their amazing (natural) hydrogen storage properties to produce clean, zero-carbon hydrogen as an abundant energy carrier. If the processes adopted use renewable energy, then this would represent the transition to a global energy future of *Green hydrogen from fossil fuels*.

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