Review

Current status of hybrid, battery and fuel cell electric vehicles: From electrochemistry to market prospects

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ABSTRACT

Decarbonising transport is proving to be one of today's major challenges for the global automotive industry due to many factors such as the increase in greenhouse gas and particulate emissions affecting not only the climate but also humans, the increase in pollution, rapid oil depletion, issues with energy security and dependency from foreign sources and population growth. For more than a century, our society has been dependent upon oil, and major breakthroughs in low- and ultra-low carbon technologies and vehicles are urgently required. This review paper highlights the current status of hybrid, battery and fuel cell electric vehicles from an electrochemical and market point of view. The review paper also discusses the advantages and disadvantages of using each technology in the automotive industry and the impact of these technologies on consumers.

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1. Introduction

Decarbonising transport is proving to be one of the largest R&D projects of the early 21st century. There are around 1 billion automobiles in use worldwide, satisfying many needs for mobility in daily life [1]. The automotive industry is therefore one of the largest economic forces globally, employing nearly 10 million people and generating a value chain in excess of \$3 trillion per year [2]. As a consequence of this colossal industry, the large number of automobiles in use has caused and continues to cause a series of major issues in our society:

- *Greenhouse gas (GHG) emissions*—the transportation sector contributes ~13.1% of GHG emissions worldwide (5 billion tonnes of CO_2 per year). More than two thirds of transport-related GHG emissions originate from road transport [3]. Reducing the GHG emissions of automobiles has thus become a national and international priority.
- *Air pollution*—tailpipe emissions are responsible for several debilitating respiratory conditions, in particular the particulate emissions from diesel vehicles. The increasing number of diesel vehicles on Europe's roads would further worsen air quality.
- *Oil depletion*—oil reserves are projected to only last 40–50 years with current technology and usage. Transport is already responsible for almost 70% of the EU's oil use and this share continues to increase [4].
- *Energy security*—Europe dependence on foreign sources for more than 80% of its oil and reserves of conventional oil are increasingly concentrated in politically unstable regions [4]; dependency on fossil fuels for transportation therefore needs to be reduced.
- *Population growth*—It has recently been declared (31/10/11) that there are 7 billion inhabitants in the world with an estimated figure of 9 billion in 40 years' time. This will obviously have an important impact on climate change, food security and energy security.

The ever increasing demand for personal mobility and near total dependence on liquid hydrocarbons means that emission reductions from this sector will be particularly difficult.

The development of alternative fuels to petrol and diesel has been ongoing since the 1970s, initially in response to the oil shocks and concerns over urban air pollution. Efforts have gained momentum more recently as the volatility of oil prices and stability of supplies, not to mention the consequences of global climate change, have risen up political agendas the world over.

Low-carbon technologies are therefore rapidly advancing, with petrol and diesel hybrids, battery electric, hydrogen fuel cell and hybrids of the two being developed by nearly every major manufacturer. Concerns about up-scaling production and the 'true' environmental and social costs of biofuels means that hydrogen and

electricity are widely regarded as the sustainable transport fuels of the future.

This review aims to highlight the current status of hybrid, battery and fuel cell electric vehicles (FCEVs) from an electrochemical and market point of view. The review paper also discusses the advantages and disadvantages of using battery, hydrogen and fuel cell technologies in the automotive industry and the impact of these technologies on consumers.

2. Energy storage devices (ESDs) for the transportation sector

ESDs are systems which store energy in various forms such as electrochemical, kinetic, pressure, potential, electromagnetic, chemical and thermal, using, e.g. fuel cells, batteries, capacitors, flywheels, compressed air, pumped hydro, super magnets, hydrogen etc. The principal criteria of an ESD required for a specific application, in this case automotive, are (i) the amount of energy in terms of specific energy (in $Wh\,kg^{-1}$) and energy density (in $Wh\,kg^{-1}$ or $Wh\,l^{-1}$), (ii) the electrical power (in $W\,kg^{-1}$ or $W\,l^{-1}$) i.e. the electrical load required, (iii) the volume and mass, (iv) reliability, (v) durability, (vi) safety, (vii) cost, (viii) recyclability and (ix) environmental impact. When choosing an ESD, the following characteristics should be considered: specific power, storage capacity, specific energy, response time, efficiency, self-discharge rate/charging cycles, sensitivity to heat, charge–discharge rate lifetime, environmental effects, capital/operating cost and maintenance. For battery electric vehicles (BEV—*see later*), batteries with stored energies of 5–30 kWh for electric cars and up to 100 kWh for electric buses are required; whereas hybrid electric vehicles (HEVs) hold 1–5 kWh of stored energy, and focus more exclusively on high power discharge. Table 1 shows several types of electrochemical ESDs and their characteristics.

2.1. Batteries

A battery is an electrochemical cell (also known as a *Galvanic* cell) that transforms chemical energy into electrical energy; it consists of an anode and a cathode, separated by an electrolyte (an ionic conductor which is also an electronically insulating medium). Electrons are generated at the anode and flow towards the cathode through the external circuit while, at the same time, electroneutrality is ensured by ion transport across the electrolyte (Table 2).

The two main types of battery used in BEVs are nickel metal hydride (NiMH) and lithium-ion (Li-ion) batteries. NiMH batteries are in most cases used as secondary energy sources in HEVs (e.g. Toyota Prius) where they are used in conjunction with an internal combustion engine (ICE), whereas Li-ion batteries are used as primary energy sources in BEVs such as the Nissan Leaf and

Table 1
Electrochemical ESDs characteristics.

Characteristics	Supercapacitors (Electrochemical capacitors)	Batteries	Fuel cells
Charge/discharge time	ms–s	1–12 h	1–300 h
Operating temperature/°C	−40 to +85	−20 to +65	+25 to +1000
Operating cell potential (ΔV)/V	2.3–2.75	1.25–4.2	0.6–1.0
Capacitance/F	0.1–2	–	–
Lifetime	30,000+ h	150–1500 cycles	1500–10,000 h
Weight/kg	0.001–2	0.001–10	0.02–10
Power density/kW kg^{-1}	10–100	0.005–0.4	0.001–0.1
Energy Density/Wh kg^{-1}	1–5	5–600	300–3000

Table 2
Characteristics of various types of battery [5].

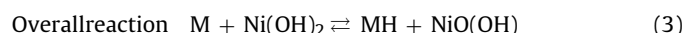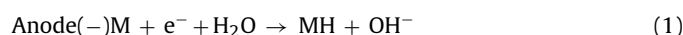| Battery chemistry	Type: primary (P) secondary (S)	Cell potential (ΔV)/V	Theoretical (practical) specific energy/Wh kg^{-1}	Useful energy density/Wh l^{-1}
Alkaline zinc manganese dioxide (Zn/MnO_2)	P	1.5	358 (145)	400
Lithium iodine (Li/I_2)	P	2.8	560 (245)	900
Alkaline nickel cadmium (NiCd)	S	1.3	244 (35)	100
Nickel metal hydride (NiMH)	S	1.3	240 (75)	240
Lead acid (Pd/A)	S	2.1	252 (35)	70
Sodium sulphur (Na/S)	S	2.1	792 (170)	345
Sodium nickel chloride ($Na/NiCl_2$)	S	2.6	787 (115)	190
Lithium-ion (Li-ion)	S	4.1	410 (180)	400

Mitsubishi iMiev (Fig. 1). The $35,000 5-door Nissan Leaf BEV is powered by 12×4 cells (48 modules) providing a capacity of 24 kWh and taking up to 8 h to fully charge from a standard domestic outlet from zero state-of-charge (SoC), or 30 min from a 3-phase AC socket.

2.1.1. Nickel metal hydride (NiMH) batteries

NiMH batteries are used in over 95% of all HEVs, and major manufacturers have so far invested substantially in the last 10 years. The major advantage from a manufacturing point of view is the safety of NiMH compared to Li-ion batteries, and, so far, no incidents have been reported in the press. Furthermore, NiMH batteries are preferred in industrial and consumer applications due to their design flexibility (e.g. ranging from 30 mAh to 250 Ah), environmental acceptability, low maintenance, high power and energy densities, cost and most importantly safety (in charge and discharge modes, especially at high voltages). NiMH batteries are currently priced at $250–$1500/kWh, hence the total price of the battery pack for a hybrid (e.g. Toyota Prius) varies anywhere between $600 and $3000 per vehicle.

The NiMH battery was patented in 1986 by Stanford Ovshinsky, founder of Ovonics, when researching hydrogen storage materials. Ovshinsky also described the NiMH as the 'hydrogen ion' or 'protonic' battery by analogy with lithium-ion batteries as the NiMH electrochemical reaction involves the transfer and 'insertion' of H$^+$. The components of NiMH batteries include an anode of hydrogen absorbing alloys (MH), a cathode of nickel hydroxide ($Ni(OH)_2$) and a potassium hydroxide (KOH) electrolyte (Fig. 2) [6].

The general electrochemical reactions are as follows:

$$Anode(-) M + e^- + H_2O \rightarrow MH + OH^- \tag{1}$$

$$Cathode(+) Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^- \tag{2}$$

$$Overall reaction \quad M + Ni(OH)_2 \rightleftharpoons MH + NiO(OH) \tag{3}$$

where 'M' is an intermetallic alloy capable of forming a metal-hydride phase.

2.1.2. Lithium-ion (Li-ion) batteries

Lithium-ion batteries are light, compact and operate with a cell voltage of ~4 V with a specific energy in the range of
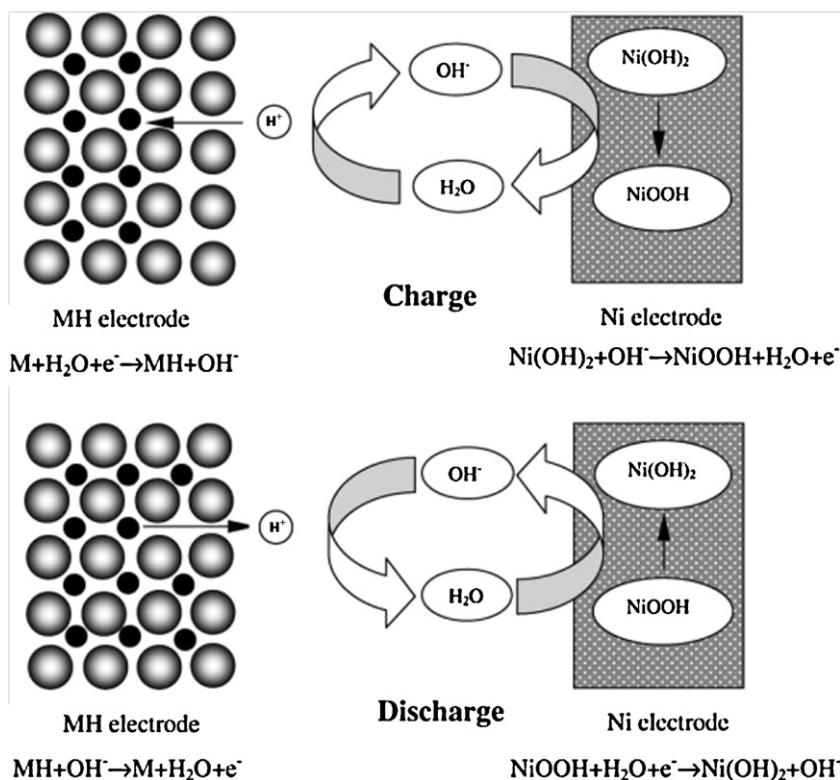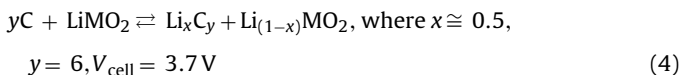

Courtesy of Nissan

Courtesy of Mitsubishi

Fig. 1. Nissan Leaf and Mitsubishi iMiev.

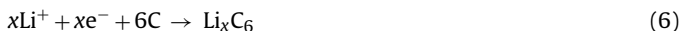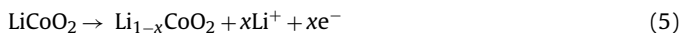*Source*: Courtesy of: Nissan Motor Company and Mitsubishi.

Fig. 2. Schematic diagram of the electrochemical reaction processes of a NiMH battery. For the charge process, the hydrogen atom dissociates from Ni(OH)$_2$ and is absorbed by the MH alloy. For the discharge process, the hydrogen atom dissociates from the MH alloy and joins with NiOH to form Ni(OH)$_2$ [6].

100–180 Wh kg^{-1}. In these type of batteries both the anode (graphite e.g. mesocarbon microbeads—MCMB) and cathode (lithium metal oxide—LMO$_2$ e.g. LiCoO$_2$) are materials into which, and from which, lithium (as Li$^+$) migrates through the electrolyte (typically a lithium salt e.g. lithium hexafluorophosphate, LiF$_6$, in an organic solvent e.g. ethylene carbonate–dimethyl carbonate, EC–DMC in a separator felt), then is inserted (intercalation process) or extracted (deintercalation process) into the electrodes (Fig. 3) [7,8].
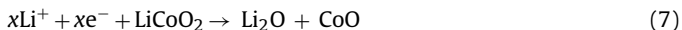
Thus when a lithium-ion battery is discharging, Li is extracted from the anode (−) and inserted into the cathode (+) and when it is charging, the reverse process occurs according to the following reactions:

$$y\text{C} + \text{LiMO}_2 \rightleftarrows \text{Li}_x\text{C}_y + \text{Li}_{(1-x)}\text{MO}_2, \text{ where } x \cong 0.5,$$

$$y = 6, V_{\text{cell}} = 3.7\,\text{V} \tag{4}$$

For the case of LiCoO$_2$:

$$\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \tag{5}$$

$$x\text{Li}^+ + xe^- + 6\text{C} \rightarrow \text{Li}_x\text{C}_6 \tag{6}$$

The overall reaction is:

$$x\text{Li}^+ + xe^- + \text{LiCoO}_2 \rightarrow \text{Li}_2\text{O} + \text{CoO} \tag{7}$$

During recharging Li$^+$ ions are removed and the oxidation of Co^{3+} to Co^{4+} occurs. The Co^{3+}/Co^{4+} couple supplies a cell voltage of about 4.0 V vs. metallic Li.

Li-ion batteries store more energy than NiMH, however they suffer from major issues such as costs (~$1000/kWh), wide operational temperature ranges, materials availability (e.g. Li), environmental impact and safety. For example, LiCoO$_2$ batteries are unsafe as they are thermodynamically unstable although they are kinetically stable in practice. It is often observed that these

batteries suffer from (i) electrolyte decomposition leading to the formation of oxide films on the anode, thus blocking extraction sites of lithium and (ii) severe oxidative processes at the cathode due to overcharging, in turn causing dissolution of protective films on the cathode and excess and continuous oxidation of the electrolyte (gas evolution).

Table 3 gives a summary of the main secondary batteries and their characteristics and Fig. 4 shows a diagram comparing the various battery technologies in terms of volumetric and gravimetric energy density [9].

2.1.3. Current issues

Lithium-ion 'chemistry' for batteries has not progressed much since their introduction to the market in the early 1990s by Sony and Asahi Kasei following the pioneering work from Whittingham, Tarascon, Armand and Scrosati [9]. Therefore, breakthroughs in lithium-ion battery technology are urgently required, with innovative, performing and durable material chemistries for both the electrodes and the electrolyte sub-components. The principal objective is to identify materials exhibiting higher performance and durability than those currently offered. Currently worldwide R&D efforts focus upon the replacement of (i) graphite and LiCoO$_2$ with alternative high capacity and low-cost materials and (ii) ethylene carbonate–dimethyl carbonate with other electrolytes which do not suffer from decomposition under oxidative regimes.

According to a report from the strategy consultancy Roland Berger [11], the supply of Li-ion batteries will exceed demand by more than 100% by 2015, in other words the market will grow from circa $1.5 billion in 2011 to over $9 billion in 2015. It is speculated that the market for Li-ion batteries in the automotive sector will reach over $50 billion by 2020 [11]. At present Li-ion batteries are expensive but it is anticipated that the price will decline rapidly and that they will be the cheapest rechargeable batteries in
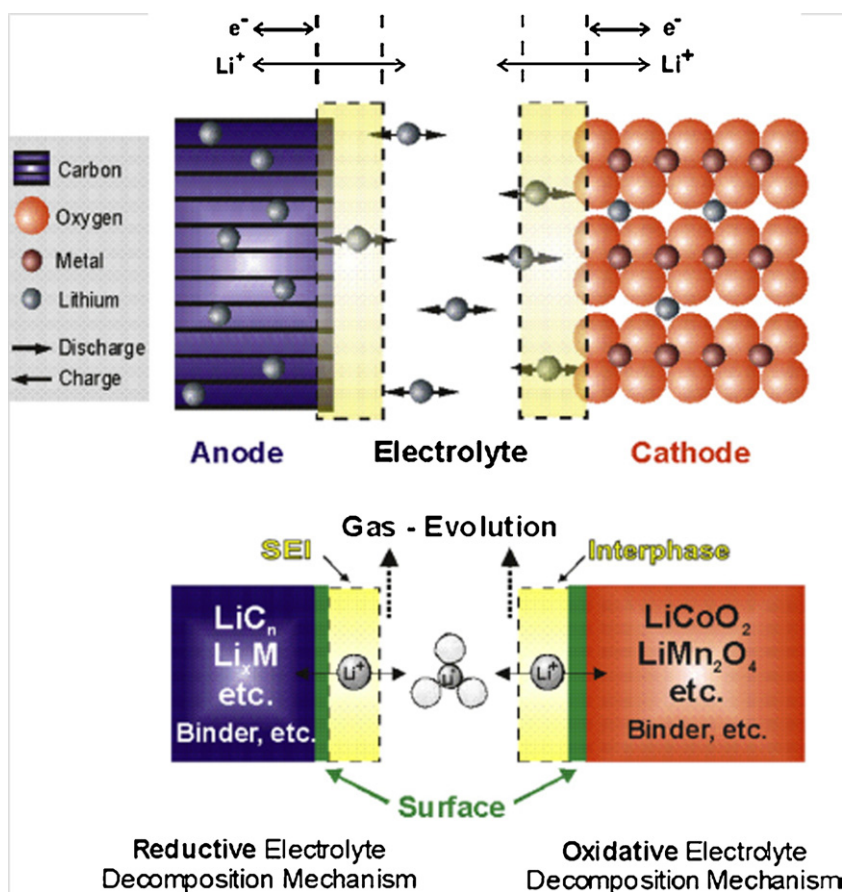
Fig. 3. Operational principle of a C/LiCoO2 Li-ion battery [7,8].

10 years time. Furthermore, the USA is supporting BEV technology with approximately $10 billion, while China is spending $15 billion on R&D for BEVs [12].

Scarcity of lithium was once thought of as a looming concern for the electrification of vehicle fleets. However, it should be noted that only around 1% of a lithium-ion battery is Li by weight, implying around 0.08 kg of Li per kWh of storage capacity (approximately 1–2 kg per BEV) [13]. At present, this lithium is not recycled due to excessive cost and energy requirements; however, if future supply shortages lead to increasing material prices, the recycling of these batteries will become standard.

2.2. Hydrogen and fuel cells

2.2.1. Hydrogen energy

2.2.1.1. Hydrogen facts, production, storage and usage. Worldwide, 50 million tonnes of hydrogen are produced, mainly through reformation of fossil fuels, with 100,000 tons of H_2 produced in the UK. Recent worldwide hydrogen production totals show that 48% of hydrogen is produced from natural gas, 30% from oil, 18% from coal and only 4% from renewable sources [14]. Nowadays, hydrogen is used in chemical processing, the petroleum industry, fats and oils, metals, electronics, space flights, utilities, glass manufacturing, etc.

Hydrogen has a the highest energy content by weight ($33,320 \, Wh \, kg^{-1}$ i.e. about 3 and 7 times more than gasoline ($12,700 \, Wh \, kg^{-1}$ or $8760 \, Wh \, l^{-1}$), natural gas ($13,900 \, Wh \, kg^{-1}$ or $5800 \, Wh \, l^{-1}$) and coal, respectively) but it has a very low energy content by volume (about 3000 times less than gasoline at STP) [15]. This makes storage and distribution to the point of use costly. 5 kg of hydrogen is equivalent to 5 gallons (or 22 l) of petrol, but to store it under ambient conditions would require a 5 m diameter vessel which is impractical!

However, the efficiency of a hydrogen ICE is ca. 25% and that of a hydrogen fuel cell vehicle is 60%; this is three times better than today's petrol-fuelled engines (18–20% for a petrol ICE reaching 40% at peak efficiency). The problem with low volumetric energy density can be increased by storing the hydrogen either under increased pressure, at extremely low temperatures as a liquid or in metal-hydride systems.
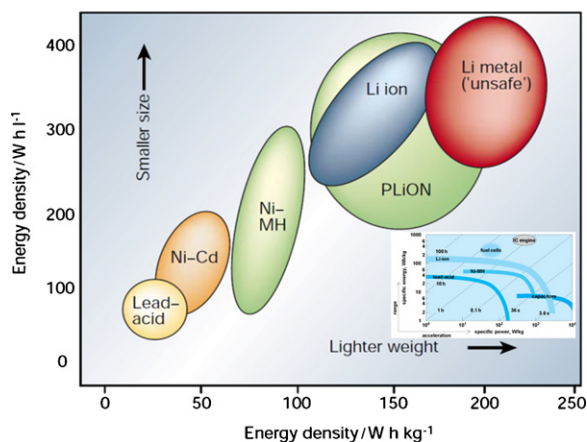

Fig. 4. Comparison of the different battery technologies in terms of volumetric ($Wh \, l^{-1}$) and gravimetric ($Wh \, kg^{-1}$) energy density [9]. Here PLiON denotes polymer lithium-ion battery. *Insert figure*: *Ragone* plot of specific power density vs. specific energy density of various electrochemical energy storage and conversion devices.

Table 3
Various secondary batteries and their reactions [10].

Battery system	Anode (−)	Electrolyte	Anodic (A) Cathodic (C) Overall (O) reactions	Cathode (+)
Lead/acid	Pb	H_2SO_4	A : $Pb + SO_4{}^{2-} \rightleftarrows PbSO_4 + 2e^-$ C : $PbO_2 + 4H^+ + SO_4{}^{2-} + 2e^- \rightleftarrows PbSO_4 + 2H_2O$ O : $PbO_2 + 2H_2SO_4 + Pb \rightleftarrows 2PbSO_4 + 2H_2O$	PbO_2
NiCd	Cd	KOH	A : $Cd + 2OH^- \rightleftarrows Cd(OH)_2 + 2e^-$ C : $2NiOOH + 2H_2O + 2e^- \rightleftarrows 2Ni(OH)_2 + 2OH^-$ O : $2NiOOH + Cd + 2H_2O \rightleftarrows Ni(OH)_2 + Cd(OH)_2$	NiOOH
NiMH	Hydrogen adsorbed alloy	KOH	A : $M + e^- + H_2O \rightleftarrows MH + OH^-$ C : $Ni(OH)_2 + OH^- \rightleftarrows NiO(OH) + H_2O + e^-$ O : $M + Ni(OH)_2 \rightleftarrows MH + NiO(OH)$	NiOOH
Lithium-ion	Li + C	Organic electrolyte + Li salt	A : $Li(C) \rightleftarrows Li^+ + e^-$ C : $Li^+ + e^- + CoO_2 \rightleftarrows LiCoO_2$ O : $Li(C) + CoO_2 \rightleftarrows LiCoO_2$	CoO_2

Hydrogen storage on board the vehicle is the key factor for achieving market success for FCEVs. To be competitive with ICE vehicles, hydrogen fuel cell vehicles should have a similar driving range. As the volumetric energy density of hydrogen is very low, storing enough hydrogen on board remains a challenge in terms of weight, volume, kinetics, safety and cost.

Methods of hydrogen storage in the vehicle are:

- *Liquid hydrogen*—the energy density of liquid hydrogen is high, but, to store hydrogen in a liquid state, it is necessary to maintain it at −253 °C at ambient pressure. Therefore a highly insulated liquid hydrogen tank is needed. Furthermore, a quarter of the chemical energy of hydrogen itself is consumed in the liquefaction process.
- *Compressed hydrogen*—the most popular method chosen by leading FCEV manufacturers. Honda and Nissan use 350 bar, whereas Toyota prefers 700 bar. The energy density is relatively low and energy is consumed in compression.
- *Metal hydride*—the safest method, but very heavy; in addition a lot of time is required to store the hydrogen (i.e. long refuelling time), and it has an insufficient release rate.
- Hydrogen absorbed onto carbon nanotubes (CNT) and metal organic frameworks (MOF)—still at developmental stage.

2.2.1.2. How is hydrogen distributed today?. Hydrogen is currently transported/stored in gaseous form using tube trailers or cylinders and in liquid form in cryogenic liquid hydrogen tankers and to a very limited extent via pipeline. Liquid hydrogen, cooled to −253 °C, is transported by road in super-insulated cryogenic tankers with capacities of up to 60,000 l. Pipelines present the most cost effective means of transporting large quantities of gaseous hydrogen over long distances. Currently the hydrogen infrastructure in the world is limited. If 40 million hydrogen fuel cell vehicles were on the road by 2030 in Europe, this would equate to 19,000 hydrogen refuelling stations, costing €6b–€24b ($8b–$33b) which is comparable to the investments made in mobile phone and broadband infrastructure.

2.2.2. Fuel cells

When oil, one of the most important energy sources in the history of mankind, was first discovered in Pennsylvania almost 150 years ago, the fuel cell had already been known for 20 years, invented by Sir William Grove, "father of the fuel cell", in 1839. Back then it was an idea that was far ahead of its time. Today, however, it is the most important development in the history of decentralised energy supply.

Today, fuel cells are widely considered to be efficient and non-polluting power sources offering much higher energy densities and energy efficiencies than any other current ESDs. Fuel cells are therefore considered to be promising energy devices for the transport, mobile and stationary sectors [16–19]. A fuel cell is an 'electrochemical' device operating at various temperatures (up to 1000 °C) that transforms the chemical energy of a fuel (hydrogen, methanol, natural gas etc.) and an oxidant (air or pure oxygen) in the presence of a catalyst into water, heat and electricity. Furthermore, the power generated by a fuel cell depends largely upon the catalytic electrodes and materials used [16–19].

There are currently six main groupings of fuel cell available [14,16–20]: (i) proton exchange membrane fuel cell (PEMFC) including direct methanol fuel cell (DMFC), (ii) alkaline fuel cell (AFC), (iii) phosphoric acid fuel cell (PAFC), (iv) molten carbonate fuel cell (MCFC), (v) solid oxide fuel cell (SOFC) and (vi) microbial fuel cell (MFC). PEMFC, AFC, PAFC and MFC operate at low temperatures in the range of 50–200 °C and MCFC and SOFC at high temperatures in the range of 650–1000 °C (Fig. 5).

The heart of a fuel cell consists of a non-conductive electrolyte material sandwiched between two electrodes—the anode and cathode [14]. The fuel and the oxidant are fed continuously to the anode and the cathode sides, respectively. At the anode side the fuel is decomposed into ions and electrons. The insulator electrolyte material allows only ions to flow from both the anode and cathode sides. The free electrons generated at the anode flow to the cathode side through an external electrical circuit. The recombination of the ions with the oxidant occurs at the cathode to form 'pure' water. In contrast to water electrolysis, the polarity of a fuel cell on the anode is negative and on the cathode is positive [14].

2.2.2.1. What is a proton exchange membrane fuel cell (PEMFC)?. PEMFC is a technology which was initially developed for military and spacecraft applications at GE (General Electric, USA) in the 1960s but was abandoned in the 1970s, due to high cost and poor durability issues. From the 1980s, a revival in PEMFC R&D occurred, particularly in industry and mainly in portable and vehicular applications with the Canadian company Ballard Power Systems. PEMFC technology has now been extended to wider applications, with the potential to power a portfolio of devices e.g. mobile phones, PDAs, laptops, cars, buses, boats, houses, telecommunication stations as well as space shuttles. In recent years, the PEMFC has been extensively demonstrated worldwide in many application fields and is now on the verge of commercialisation.

A single cell PEMFC consists of a membrane electrode assembly (MEA) sandwiched between two flow field (FF) plates (or bipolar plates if in a PEMFC stack) as shown in Fig. 6. Each cell produces ~1.1 V, so to obtain the required cell voltage, the single cells are combined to produce a PEMFC stack.

The MEA is typically made of (i) a proton exchange membrane (PEM) material (a semi-permeable ionomer with a perfluorinated
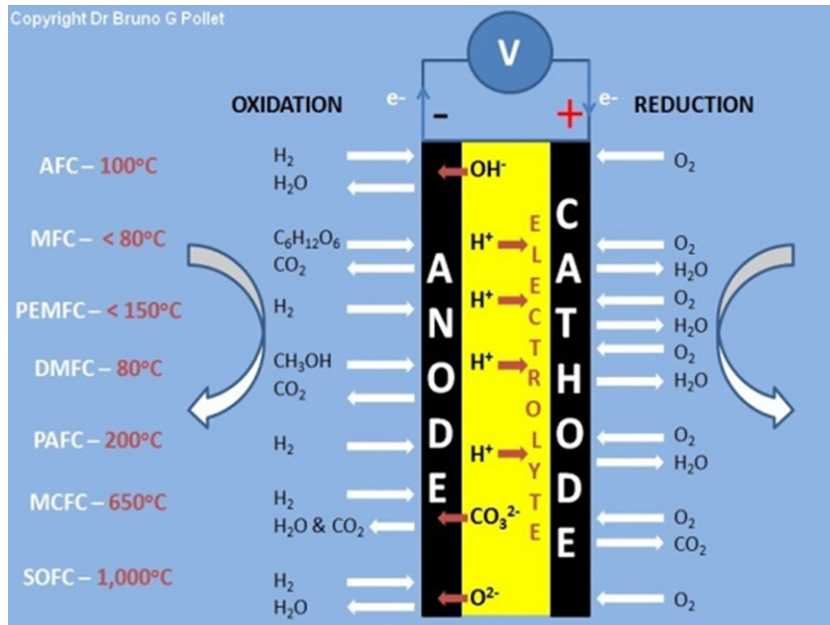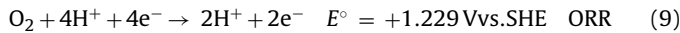
**Fig. 5.** Schematic representing all available and existing fuel cells.

backbone like Teflon e.g. Nafion® designed to conduct protons (H+)); (ii) anode and cathode electrodes or catalyst layers (CLs) made of an electrocatalyst (EC) supported on carbon and PEM material (mainly ionomer) and (iii) gas diffusion layers (GDL—allowing reactants to diffuse to the active sites on the EC and facilitating water management by allowing water vapour to diffuse out, and allows the liquid water produced on the cathode side to flow out of the fuel cell). The EC in the MEA has an important function; the electrochemical reactions involved are the electro-oxidation of hydrogen or HOR at the anode:

$$H_2 \rightarrow 2H^+ + 2e^- \quad E° = 0.000\,V\,vs.SHE \quad HOR \tag{8}$$
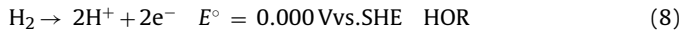
and the electro-reduction of oxygen or ORR at the cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H^+ + 2e^- \quad E° = +1.229\,V\,vs.SHE \quad ORR \tag{9}$$

where $E°$ are the standard reduction potentials (SRPs) or *formal* potentials vs. the standard hydrogen electrode (SHE reference). Thus the overall reaction is:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad E° = +1.229\,V\,vs.SHE \tag{10}$$
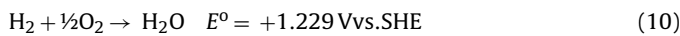
The oxygen reduction reaction (ORR) at the cathode is a kinetically slow process, which has a more dominant effect on the performance of the PEMFC than the hydrogen oxygen reaction (HOR). Consequently, developing active catalysts for the ORR is the focus of PEMFC electrocatalysis R&D. Currently a few approaches are underway to address the issues of the sluggish ORR activity, high cost and poor stability (see later).

2.2.2.2. Cost, performance and scarcity. As all fuel cells are normally distinguished by the materials used e.g. the electrolyte and catalyst materials, although the manufacturing of the fuel cell electrodes is also different in each case, the main objective in fuel cell technologies is to develop low-cost, high-performance and durable materials. As well as reducing the cost, the main target in automotive PEMFC is to operate the system above 100 °C with low humidification of reactant hydrogen and air. Large-scale deployment of PEMFCs for the transportation sector demands the development of low-cost high-performing MEAs.

Currently, fuel cell systems are too expensive and not durable [19]. Platinum (Pt) is the key catalytically active component in
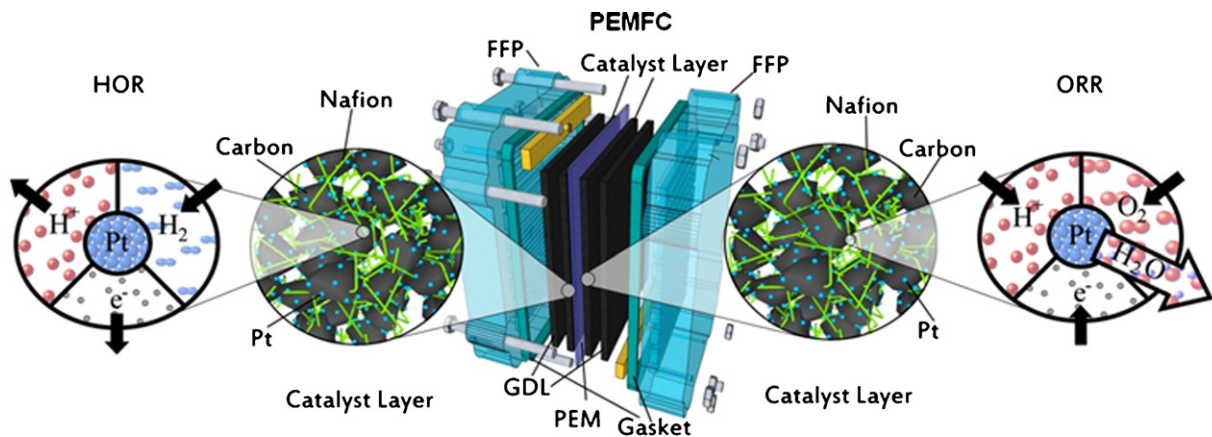
Fig. 6. Layout of a single cell PEMFC.

three of the six main fuel cell types (PEMFC, DMFC and PAFC) currently being used commercially in portable, stationary and transport applications and platinum offers benefits in terms of activity and selectivity over novel alternative materials. However, several avenues have been explored with the aim to reduce the cost and increase the performance of fuel cells. These can broadly be listed as [14,16–20]:

(i) Reducing the EC loading in fuel cell electrodes;
(ii) Developing novel nanostructured thin-film structures (e.g. 3M's NSTF electrode);
(iii) Decreasing the EC nanoparticle size;
(iv) Reducing Pt dependence by developing metallic alloy (either as binary and ternary) and Pt-free ECs;
(v) Improving EC dispersion by using novel fabrication methods;
(vi) Developing MEA fabrication methods to enable better catalyst dispersion and utilisation;
(vii) Using new techniques to increase mass-transport at the fuel cell electrode surface and
(viii) Improving the performance of carbonaceous EC support and exploring novel non-carbonaceous EC support materials.

Although the degradation of platinum is now well understood, there are a few solutions under investigation to prevent this important effect. For example, many researchers have successfully modified platinum with gold or other base metals, optimised its crystallographic structure and modified as well as strengthened the support material–catalyst interaction.

The automotive industry is a major user of Pt, particularly for diesel ICEs, and it has always aimed at reducing or removing its use in catalytic converters. Although Pt loadings in PEMFCs have reduced by more than 80% in the last 10 years or so, the other major issue is the high-cost of the precious-metal catalyst (~$60/g on 14/03/2012). Pt contributes approximately one-third of the stack cost [21], down from over half in 2008 [22]. Major automotive manufacturers such as Honda (FCX Clarity), Nissan (FCV X-trail), Hyundai, Daimler-Chrysler etc. have spent large R&D investment in 'pure' FCEVs [up to 100 kW at ca. $300,000 (DoE website)] for demonstration and with a price-tag of up to $2 million. Many sceptics believe that 'pure' FCEV is not the way forward for two main reasons: (i) high cost of manufacturing and components and (ii) availability of components. For example, if 600 million 'pure' FCEVs running at 100 kW were produced worldwide, ca. 12,000 tonnes of platinum (Pt) would be required. In other words, the platinum industry has the potential to meet the requirements of a scenario where FCEVs achieve 50% market penetration by 2050, while 80% market penetration could exceed the expansion capabilities of the industry, assuming a DoE R&D target of 0.2 g/kW by 2015. To achieve FCEV sale volumes of, e.g. 500,000 units per year using Pt catalyst, an additional 8 tons will have to be produced for the new units, assuming the 2015 US DoE target is met and assuming that the 0.2 g will work well in a 100 kW system (Fig. 7). Furthermore, unless the Pt can be economically recycled to the purity needed, additional Pt will have to be mined to replace the platinum in the refurbished fuel cells in the existing fleet.

However, from an 'electrochemical point of view', Pt is still the best EC for PEMFC as it is stable, 'durable' and very active towards the HOR and the ORR. There have been many attempts at developing non-precious ECs to replace Pt [23–25]. Although promising in the laboratories, the new nanomaterials have shown poor durability and stability in acidic and aggressive environments and cell voltage cycling i.e. under 'real' operating conditions (although it has been shown that iron-based nanostructures on nitrogen functionalised mesoporous carbons have exhibited durability and stability comparable to Pt alone).

In addition to the high material cost, the precious-metal Pt catalyst is extremely sensitive to poisoning by CO, H_2S, NH_3, organic sulphur–carbon and carbon–hydrogen compounds in the H_2 stream and NO_x and SO_x in air. Pt is also prone to dissolution and/or agglomeration resulting in performance degradation. More significantly, Pt is rare and is mined in a limited number of countries worldwide, with >80% mined in South Africa. Pt deposits are likely to become scarce in the coming years [~40 years reserves at the present rate]. However, other minerals have historically seen a "falsification" of resource scarcity, as the quantity of known reserves tends to increase in line with, or in excess of, increases in the rate of consumption due to economic factors [26].

In the last five years, platinum utilisation in automotive stacks has increased five-fold to over 5 kW g^{-1} of PGM. General Motors, e.g. have reduced platinum usage in their newest generation of fuel cell stack from 80 g down to 30 g, and believe they can achieve platinum loadings of 10 g by 2020 [12].

This compares more favourably with platinum usage in conventional ICE vehicles of around 4–5 g (1 g for petrol, 8 g for diesel) for the catalytic converter [27]. Around 70 tonnes of platinum are used by the EU auto industry each year; however, loadings are decreasing due to soaring metal costs, and the risk of opportunistic theft of catalytic converters. Uptake of FCEVs will certainly increase demand for platinum, but not by an unfeasible amount.

2.2.3. Hydrogen and fuel cell challenges

Hydrogen and fuel cell technologies have been identified as priorities for direct investment by many governments such as those of the UK and other EU countries. These technologies will contribute to tackling the UK/EU climate change targets (80% reduction in CO_2/GHGs by 2050) and energy security, whilst providing significant market opportunities to a strong UK/EU capability base. Many governments have set targets for fuel cell and hydrogen technologies e.g. increasing durability and performance levels up to 8000 h for transport applications and 40,000 h for stationary applications with target costs of longer term sustainable hydrogen below €5/kg ($6.80/kg). The expected impact will be through a breakthrough in materials bringing costs towards commercial cost and performance targets of €45/kW ($62/kW) (mobile applications) and €1500/kW ($2000/kW) (small-scale stationary applications) with power density above 1 W cm^{-2} (2015 US DoE target, see Fig. 7).

There are a few challenges related to hydrogen generation, storage and utilisation and governments, together with academic and industry researchers, are currently looking to tackle them. These include: (a) the design and development of low-cost and efficient hydrogen production systems using novel technologies, with a particular emphasis on the production of 'green' hydrogen from renewable sources (biomass, biowaste, electrolysers powered by photovoltaic and wind energy systems etc.); (b) novel technologies associated with low carbon emission hydrogen production and utilisation from fossil fuels (including hydrogen separation technologies) and distributed hydrogen technologies (in terms of transport, this would include innovative on-site vehicle refuelling systems); and (c) the development of novel systems, materials and solutions for hydrogen storage and transportation, with low costs and high energy efficiency (with a focus on systems offering storage solutions suitable for integration with HFC vehicles).

2.3. Electrochemical capacitors

Electrochemical capacitors (EC), also called supercapacitors or ultracapacitors are high-energy-density devices. There are two energy storage mechanisms for ECs: (i) electrochemical double
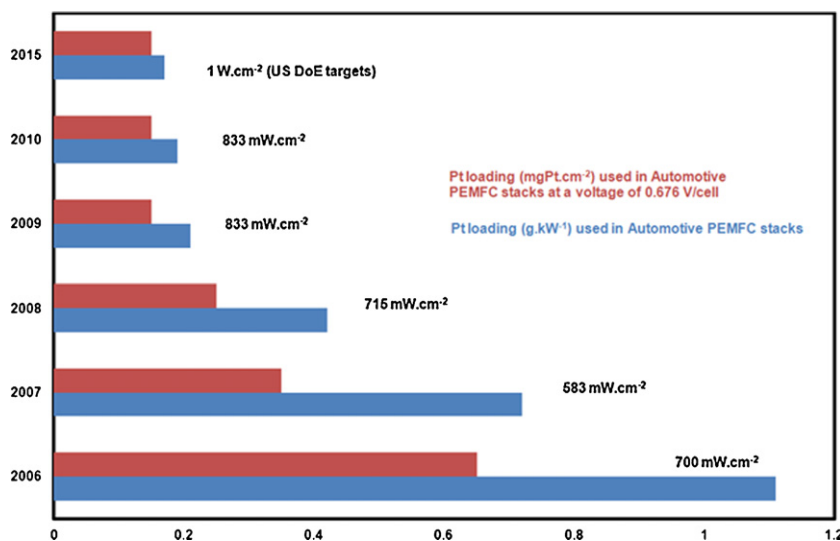
Fig. 7. Evolution of total platinum loadings and power densities in PEMFC stack.

layer capacitors (EDLC) i.e. double-layer capacitance arising from the charge separation at the electrode/electrolyte interfaces—they consist of activated carbon with high specific area as electrodes and an organic electrolyte able to reach a specific capacitance in excess of $7000\,F\,kg^{-1}$ (or $9000\,F\,l^{-1}$) [28] and (ii), pseudo-capacitors i.e. pseudo-capacitance arising from fast, reversible *faradaic* reactions occurring at or near solid electrode surfaces—they contain transition metal oxides, nitrides and polymers possessing relatively high surface areas (1500–$2400\,m^2\,g^{-1}$), such as hydrous RuO_2, Fe_3O_4, porous NiO_x, CoO_x, MnO_2 and SnO_2 as electrode materials [29]. The use of RuO_2 for pseudo-capacitors has been extensively investigated as it is highly conductive, possessing three oxidation states $<1.2\,V$ with fast electron transfer. The process involves fast kinetics and H^+ adsorption on RuO_2 where the Ru varies from Ru^{2+} to Ru^{4+} according to equation (11) [29]:

$$RuO_2 + xH^+ + xe^- \quad RuO_{2-x}(OH)_x \text{ where } x = [0\text{–}2] \qquad (11)$$
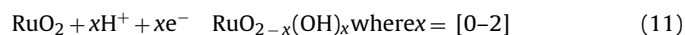
The change of x during the entry or exit of H^+ occurs at a potential of c. $1.2\,V$ which leads to a capacitive behaviour with ion absorption of the *Frumkin isotherm* type with specific capacities $>600\,F\,g^{-1}$. Due to the high cost of Ru-based ECs and their limitations, i.e. a maximum cell voltage of $\sim1.0\,V$ (ideal for small electronic devices), ECs based on MnO_2 have been studied as they offer higher specific capacities ($\sim150\,F\,g^{-1}$) and are cheaper [29].

In all cases, ECs rely upon the separation of chemically charged species at an electrified interface between a solid electrode and an electrolyte. The electrolyte between the anode and cathode is ionic (usually a salt in an appropriate solvent). The operating cell voltage is controlled by the breakdown voltages of the solvents (i.e. the decomposition cell voltages) with aqueous ($1.1\,V$) and organic electrolytes (2.5–$3\,V$).

ECs are currently being proposed by many automotive manufacturers (VW, Honda, Toyota, Nissan, Hyundai etc.) for HEVs, BEVs and FCEVs to (i) load level energy demand, (ii) quickly inject or absorb power to help minimise voltage fluctuations in the electronic systems and (iii) provide pulse power well over $1000\,W\,kg^{-1}$ with a cycle life reaching more than 500,000 cycles. When ECs are fully charged or discharged in seconds their energy density may reach up to $\sim5\,Wh\,kg^{-1}$ and higher power delivery or uptake, up to $10\,kW\,kg^{-1}$, can be achieved in a few seconds. In contrast to batteries and fuel cells, the lifetime of ECs is virtually 'indefinite' and in some cases their energy efficiency rarely falls below

90% provided they are kept within their design limits. Only ECs can provide a combination of high power density and relatively high energy density. However, unlike batteries and fuel cells, almost all of this energy is available in a *quasi*-reversible process (Fig. 8).

Finally, it is speculated that the next generations of ECs are expected to come close to Li-ion battery technologies in energy density while maintaining their high power density. This will only be possible if (i) room temperature ionic liquids (RTIL) with a voltage window of more than $4\,V$ are used and (ii) novel nanomaterials combining both double-layer and pseudo-capacitance are discovered [29].
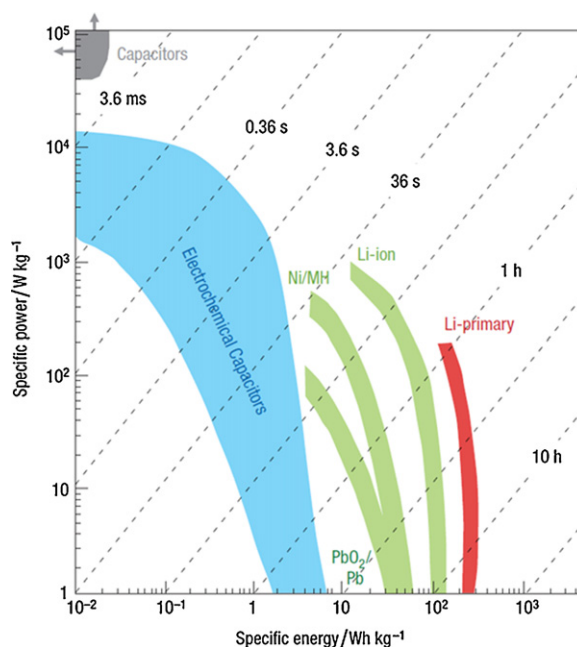
Fig. 8. Specific power ($W\,kg^{-1}$) against specific energy ($Wh\,kg^{-1}$), also called a *Ragone* plot, for various electrical energy storage devices. If a supercapacitor is used in an electric vehicle, the specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge. Times shown are the time constants of the devices, obtained by dividing the energy density by the power [29].
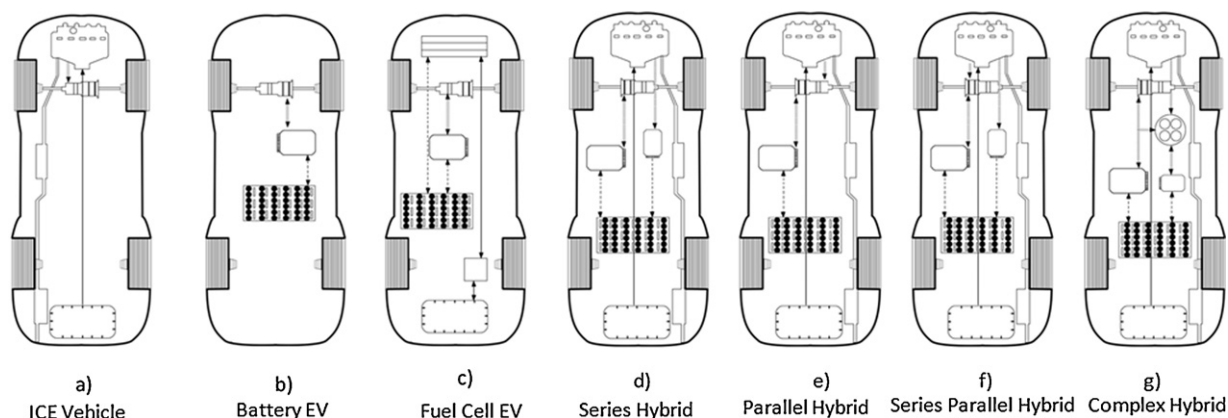
Fig. 9. Schematic drawings of seven types of vehicles: (a) ICE vehicle; (b) battery electric vehicle; (c) fuel cell electric vehicle, (d) series hybrid vehicle; (e) parallel hybrid vehicle; (f) series–parallel hybrid vehicle and (g) complex hybrid vehicle.

3. Current status of low-carbon vehicle technologies

Many automotive manufacturers have now shifted their research effort to focus on high energy efficiency and renewable energy vehicles due to the problems caused by conventional vehicles. There are numerous potential solutions to eliminating these problems, such as hybrid vehicles, bio fuel vehicles, BEV and FCEVs. Currently there is no clear answer as to which one could dominate the future low carbon vehicle market. McKinsey (2010) states that many automobile companies have an equal interest in all four power-trains and scholars broadly agree that all currently viable technologies are likely to play a part in a future sustainable transport system [30,57].

3.1. Conventional ICE vehicles

The IC engine powered vehicle (Fig. 9(a)) is one of the greatest achievements in human history; the design has been perfected over 150 years and become the most popular power plant for vehicles. This is because the ICE vehicle had one dominant feature; it used petrol/diesel as a fuel, and so had a range that was far superior to other vehicles, for instance, battery vehicles. This can be explained by the energy density of petrol/diesel fuel compared to batteries, see comparison chart Ragone plot (Fig. 4).

The IC engine dominated and will continue to dominate automobile technology for many years, even in today's most advanced hybrid vehicles the ICE is still the first choice as the main power supply. However the hybrid vehicle's ICE is different from the conventional vehicle's ICE: the engine in the hybrid vehicle is normally smaller and runs at its high efficiency point for longer periods of time, hence achieving better fuel economy.

Continuing to improve the efficiency of ICE is still the primary task for automotive engineers; some popular methods of improvement such as engine downsizing have doubled engine efficiency over the last 20 years. However, most engines are still not equipped with the most efficient technologies such as turbo chargers or variable valve timing, mainly because of their increased cost.

3.2. Hybrid electric vehicles (HEV)

Broadly speaking, a hybrid vehicle power-train can combine any two power sources. Possible combinations include but are not limited to diesel/petrol ICE with a battery, capacitor or flywheel, or fuel cell with a battery or capacitor. Typically one component is for storage and the other is for the conversion of a fuel into usable energy.

3.2.1. Why hybrids?

Conventional vehicles with ICE provide good performance and long operating range by combusting liquid fuels, with the advantage of high energy density. However, conventional ICE vehicles have the disadvantages of poor fuel economy and environmental pollution. The main reasons for their poor fuel economy are:

- Mismatch of engine fuel efficiency characteristics with real-world driving conditions;
- Waste of vehicle kinetic energy while braking, especially when driving in urban conditions;
- Energy wastage during engine idling and standby;
- Low efficiency of hydraulic transmission (automatic) in current vehicles under stop-and-go driving conditions.

BEVs on the other hand possess some advantages over conventional ICE vehicles, such as high energy efficiency and zero tailpipe emissions. However, the limited range and long time charging makes them far less competitive than ICE vehicles, due to the much lower energy density of the batteries compared to liquid fuels. HEVs, which combine the best features of the two power sources, gain the advantages of both ICE vehicles and BEVs, and overcome their individual disadvantages. HEVs are more expensive than conventional vehicles because of the extra components and complexity required, but less expensive than BEVs due to the high cost of batteries.

3.2.2. Architectures of hybrid electric drive trains

There are four common design options: series, parallel, series–parallel and complex hybrid. In any HEV, there are two forms of energy flowing through the drive train: mechanical energy and electrical energy. Adding two powers together or splitting one power into two at the power merging point always involves a single form of power (i.e. electric or mechanical) [31].

3.2.2.1. Series hybrid. Fig. 9(d) shows the series hybrid configuration, which is the simplest kind of HEV, also called the range extender hybrid. The IC engine's mechanical power is firstly converted into electrons using a generator; the converted electricity either charges the battery pack or supplies the electric motor directly for traction. Theoretically, the IC engine plays the role of a charger, continuously replenishing the battery pack, and since there is no mechanical connection between the engine and the driven wheels, it can operate at the peak efficiency point continuously, even when the vehicle is at a standstill, therefore improving the engine's thermal efficiency. One example of series hybrid vehicle is the Chevrolet Volt.

3.2.2.2. Parallel hybrid. Fig. 9(e) shows the parallel hybrid configuration. In contrast to the series hybrid, the parallel HEV allows both the engine and the electric motor to deliver power in parallel to drive the wheels. Since both the engine and electric motor are generally coupled to the drive shaft of the wheels via two clutches, the propulsion power may be supplied by the engine alone, by the electric motor alone or by both. It is inherently an electric-assisted ICE vehicle. In order to achieve both lower emissions and fuel consumption, the electric motor also acts as a generator to charge the battery when braking, or when the IC engine output is greater than that required to drive the wheels. Compared to series hybrid, parallel hybrid needs fewer propulsion devices, and a downsized ICE and smaller motor can be used. A good example is the Honda Insight.

3.2.2.3. Series–parallel hybrid. In the series–parallel hybrid, the configuration (as shown in Fig. 9(f)) incorporates the features of both the series and parallel HEVs, but involves an additional mechanical link compared with the series hybrid and also an additional generator compared with the parallel hybrid. Although possessing the advantageous features of both the series and parallel HEVs, the series–parallel HEV is relatively more complicated and costly. Nevertheless, with the advances in control and manufacturing technologies, some modern HEVs prefer to adopt this system.

3.2.2.4. Complex hybrid systems. As reflected in its name, this system involves a complex configuration that cannot be classified into the previous three configurations. As shown in Fig. 9(g), in series–parallel hybrid, the generator and electric motor are both electric machinery. However, the key difference lies in the bidirectional power flow of the electric motor in the complex hybrid and the unidirectional power flow of the generator in the series–parallel hybrid. Like the series–parallel HEV, the complex hybrid suffers from higher complexity and costliness. Nevertheless, some newly introduced HEVs have adopted this system, such as the Toyota Prius.

3.3. Battery electric vehicles (BEV)

3.3.1. History

The first BEV was built by Thomas Davenport in 1834; even a few decades earlier than the first ICE vehicle. The first vehicle to surpass the 100 km/h barrier was also a battery vehicle, namely the 'Jamais Contente' which was driven by Camille Jenatzy in 1899 [32]. In comparison with ICE vehicles, BEVs were comfortable, quiet and clean. However, due to the limited energy storage capacity of the battery, the range was very limited, and at the same time, the ICE was improving dramatically. As a consequence, the BEV almost vanished by the 1930s [33]. But, due to the energy crisis and oil shortage in the 1970s, automakers and policy makers started to re-think the BEV, as it offered high energy efficiency and allowed the diversification of energy resources, as well as having zero local emissions and helping to improve urban air quality.

3.3.2. Current status

Battery vehicles use an electric motor for traction instead of an ICE, and use batteries for their energy source instead of liquid fuels, as shown in Fig. 9(b). BEVs have many advantages over conventional ICE vehicles, such as no tailpipe emissions, high efficiency and potential for independence from fossil fuels and quiet and smooth operation. The characteristics of the BEV and HEV battery packs are very different. The BEV battery pack has high specific energy while the HEV battery pack has high specific power. Since the motor in a power-assist (grid-independent) HEV is used intermittently and must be capable of producing high power for short periods of time (e.g. during maximum acceleration), its battery pack should be optimised for high power.

The battery vehicle drive train consists of three major subsystems:

- Electric motor propulsion system—vehicle controller, power electronic converter, the electric motor and transmission;
- Battery system—batteries, Battery Management System (BMS) and charging unit;
- Auxiliary system—heating/cooling, electronic pumps and other electronic auxiliaries.

The principle of the BEV is very straight forward, based on the control inputs from the accelerator and brake pedals, the vehicle controller provides proper control signals to the electronic power convertor, which functions to regulate the power flow between the electric motor and battery. The motor can also play the role of a generator, converting the braking energy to electrons and charging the battery. The energy management unit cooperates with the vehicle controller to control the regenerative braking and its energy recovery. The electric motors produce a great amount of torque from rest to give amazing performance. In terms of acceleration and power, BEVs are superior to IC vehicles.

3.3.3. Future developments

While significant progress has been made in developing automotive batteries, major challenges remain, as follows:

- Reducing cost—Currently a Li-ion battery with 35 kWh storage capacity costs around $30,000 to manufacture, while a few organisations (ANL, IEA, EPRI
- CARB) project future prices around one-third of this. Reducing the cost of battery packs is therefore the key challenge for BEV development [34].
- Improving safety—Current nickel and cobalt-based oxide Li-ion cathode materials have potential issues with overcharging, clearly, and voltage control at cell, module and battery level is critical to prevent overcharging of automotive Li-ion batteries, but these are all factors that will inevitably increase Li-ion battery cost further. Lithium iron phosphate cathodes offer a promising future but with lower specific energy and power density.
- Prolonging the life-span—as an automotive battery, it should last at least 10 years or 150,000 miles under a variety of conditions, whereas e.g. the current average life of vehicles registered in the UK is 14 years.
- Shortening the charging time to a matter of minutes, and providing better charging facilities.
- Reducing the size and weight of the battery pack.

Compared with the problems posed by batteries, the challenges for the motor/controller for electric vehicles may seem relatively small, with remaining developments aimed at improving the efficiency and reliability.

3.4. Fuel cell electric vehicles (FCEV)

3.4.1. Introduction

FCEVs share many of the same components as BEVs, such as electric motors and power controllers or inverters; however, the major difference is the main energy source, see Fig. 9(c). While BEVs use energy stored in the battery, FCEVs use fuel cells as they are superior to batteries in many ways. The major advantages are that fuel cells are lighter and smaller and can produce electricity as long as the fuel is supplied. Due to the clear similarities between batteries and fuel cells, both these technologies will coexist in the future,

while the BEV is suitable for short range and small vehicles, the FCEV is suitable for medium–large and long-range vehicles.

The PEMFC is the best choice for automobile use. The principle of how FCEVs work is simple; they use low temperature fuel cells to generate electricity from hydrogen; the electricity is then either used to drive the vehicle or stored in an ESD, such as batteries or ultracapacitors. Since fuel cells generate electricity from chemical reactions, they do not combust fuel and therefore do not produce pollutants and produce much less heat than an ICE. The by product of a hydrogen fuel cell is water. Fuel cells have no moving parts or irregular shapes, so they have the potential for high reliability and low manufacturing cost.

Although FCEVs possess many advantages, they also have certain limitations; these relate to the fuel cell stack itself and its fuel: hydrogen production, transportation and storage.

3.4.2. PEM fuel cell stack

The PEM fuel cell stack is like the 'engine' in a conventional vehicle, which is the most important part. PEM fuel cell technologies have been developing at a good pace recently, however, two key limitations still remain: cost and durability. The cost of an ICE power plant is about $25–35/kW, but current fuel cell systems are estimated to be about five times more expensive, even taking into account cost savings for high-volume manufacturing [35]. This is because materials and manufacturing costs for catalysts, bipolar plates, membranes and GDLs are currently too high. On the other hand, the fuel cell stack as an 'automotive engine' is expected to be as durable and reliable as current automotive engines, i.e. 5000 h lifespan or 150,000 miles equivalent under a range of operating conditions, including different temperatures and climates.

3.4.3. Hydrogen as fuel for fuel cell hybrid

Fuel cells prefer to operate in a consistent condition and achieve their maximum efficiency at partial load. However, a vehicle requires a variety of power outputs according to the road and traffic conditions. Hybridisation of a fuel cell with peak power sources (PPS) could solve these problems. For instance, by using batteries or ultracapacitors when power demand is high, such as with higher loads or acceleration, PPS could help the fuel cell to provide the boost while power demand is low, such as during deceleration or when travelling downhill. The extra energy can be replenished to PPS; this allows the fuel cell system to be operated more efficiently. On the other hand, a smaller fuel cell can be used, for instance, to maintain a vehicle at 70 mph continuously requires 15 kW at the wheels, so a 20 kW fuel cell stack should able to cope with this.

So a hybrid fuel cell with a PPS could offer a viable solution for electric vehicles. Such a configuration will offer the following advantages compared to full fuel cell vehicles:

- Smaller fuel cell means lower cost;
- Fuel cell could operate at optimum efficient point most of time under appropriate control strategy;
- Fuel cell life will be extended;
- The fuel cell designer will be able to optimise the cells for power instead of cycle life;
- Deep discharging from the battery will be eliminated; therefore improving the batteries' life;
- Allows fast start-up of the fuel cell;
- Allows capture of regeneration energy.

The disadvantages of hybridisation are the complexity of the vehicle system, weight increase, complexity of the control system and extra battery cost.

3.4.4. Future development

- Reducing the cost of hydrogen—the cost of hydrogen, which includes the cost of production and delivery, has to be competitive with conventional fuels.
- Improving hydrogen storage technology—the low volumetric energy density of hydrogen makes storage a challenge. The storage needs to meet vehicle packaging, cost and performance requirements.
- Reducing fuel cell cost and improving durability—the cost of fuel cell power systems has to be reduced and durability must be improved for fuel cells to compete with conventional technologies.

3.5. Comparisons

Table 4 compares the different types of vehicles in terms of cost, performance and CO_2 emissions; here the models chosen are representative vehicles within their class, and represent the most advanced technologies to date.

4. Technical prospects and barriers

Many of the technical advantages and limitations of batteries, fuel cells and capacitors are rooted in the fundamental electrochemical mechanisms they employ. It is unlikely that the performance of these three technologies will ever converge, and so their suitability for particular applications will always remain different [36].

4.1. Cost

Upfront cost is a key factor for public acceptance and uptake, and is proving to be one of the steepest challenges for electrochemical energy systems. These alternative technologies must overthrow a century of refinement and extreme economies of scale that ICEs benefit from.

The advantage these nascent technologies possess is that, while still in their early years, technological progress has been impressive and enabled costs to fall rapidly. Toyota reports to have cut the cost of making its fuel cell vehicles by 90% since 2005, from $1 million per vehicle down to around $100,000. They expect to halve their current costs before retail sales begin in 2015 [37].

Major organisations share a common view on the pace of fuel cell cost reductions—centred around $75,000 at the start of commercialisation in 2015; under $50,000 after 5 years; and a floor level of around $30,000 by 2025 [12]. Battery prices are expected to fall less rapidly, by 50% within 10 years compared to 75% for fuel cells. By 2020, a 25 kWh battery pack is expected to cost $6000–10,000, giving a similar premium over conventional vehicles as FCEVs [12].

These costs are still a long way off $1000 for the IC Engine they replace; however, they represent only a modest increase in the cost of a complete vehicle, and are widely thought to be low enough to encourage the development of a substantial vehicle market.

4.2. Durability and degradation

The prospects for capacitors are excellent in this respect, with calendar lifetimes measured in decades and charge/discharge cycles in the millions. The calendar life of lithium-ion batteries is still a problem, as the rate of capacity loss has not improved in 7 years, at approximately 5% per year [38,39].

Lifetimes for lithium-ion chemistries are in the order of 2,000 cycles to 80% depth of discharge (DoD) before 20% of power is lost. The number of cycles is approximately reciprocal with the DoD, meaning that ~4000 cycles to 40% DoD can be expected. With the

Table 4
Comparison of vehicle specifications from a consumers' perspective.

	ICE (VW GOLF 1.4TSI)	Hybrid (Toyota Prius III)	BEV (Nissan Leaf)	FCEV (Honda FCX Clarity)
Power supply	IC engine	ICE, electric motor	Battery and electric motor	PEM fuel cells and electric motor
Fuel	Petrol, diesel and alternative fuel	Petrol/diesel as main fuel	'Electricity'	Hydrogen
Top speed (mph)	124	112	94	100
Acceleration (s)	9.5	10.4	7	10
Range (miles)	552	716	73–109	240
Purchasing price	$29,400	$33,400	$41,250 (including $8,000 government incentive)	$80,000 (estimated)
Running fuel price (per mile)	$0.22	$0.14	From $0.02	From $0.07
Fuel economy (mpg or mpg equivalent)	45.6	72.4	99	81
Tailpipe CO_2 Emission (g/km)	144	89	0	0

75 mile range of current BEVs, this suggests that the battery should last for at least 100,000 miles, comparable to an ICE. This level of durability has not yet been verified for lithium-ion chemistries, but has been obtained in real-world usage of NiMH battery packs produced some 14 years ago [40].

Fuel cells lifetimes are assessed by the number of hours until 10% power is lost. The latest generation of FCEVs from Ford, Daimler and GM are projected to last 800–1100 h, falling short of the DoE's 2009 target of 2000 h [41]. Based on these vehicles' driving patterns around California, this corresponds to 21,000–28,000 miles, and so a five-fold improvement in durability is required to compete with battery technologies. The reliability of current FCEVs must also be improved, as some vehicles are seen to lose 10–25% performance within the first 300 h of driving (~8000 miles) [41].

4.3. Energy and power density

Energy density is often cited as the largest problem for electrochemical storage devices. The specific energy and energy density of batteries and capacitors are unlikely to ever compete with liquid hydrocarbons holding around 12 kWh kg^{-1} [15].

This is, however, an unfair and misleading comparison. While the fuel in a conventional vehicle weighs relatively little by itself, plenty of additional equipment is required to convert petrol into motion: an engine, radiator, transmission system, fuel delivery lines, an exhaust and catalytic converter. In contrast, the batteries of an electric vehicle comprise the majority of the power-train mass, as the motor, wiring and transmission are relatively small, light systems. FCEVs lie in between the two extremes, as the fuel cell stack and its ancillaries are a similar weight and volume to the high pressure storage tank.

A second issue is that of conversion efficiency. The 'value' of hydrocarbons, hydrogen and electrons lies in how much of their energy can be converted into a useful form of energy, namely motion at the wheels, as this determines the range of the vehicle and cost per mile travelled. Modern combustion engines (without hybridisation) are approximately half as efficient as a practical fuel cell engine, and a quarter as efficient as battery charge–discharge cycles.

Table 5 demonstrates the impact that system weight and conversion efficiency have on the specific energy of petrol, hydrogen and lithium-ion batteries, using data from four modern vehicles. In all cases, the effective specific energy is substantially reduced from the values that are typically reported.

In order to compete with conventional vehicles in terms of "usable energy density" and thus offer a similar driving range, batteries require a five-fold increase in specific energy, while hydrogen only requires a 30% improvement. A better battery that could hold 666 Wh kg^{-1} at the cell level, or a hydrogen tank that held 6 wt.% would therefore give comparable performance from the driver's perspective.

Hydrogen has strong potential to meet this target, as "Type 4" all-composite compressed hydrogen tanks are currently approaching 5.2 wt.% at 700 bar [42]. Cryo-compressed hydrogen can presently attain 6–8 wt.%; however, it suffers from a significant energy cost of liquefaction. Several forms of metal-hydride storage are also on the horizon, with ammonia–borane (AB) complexes and metal-organic frameworks (MOF-5) also expected to exceed 6 wt.% [42]. Toyota is targetting 8 wt.% storage by 2015, using a hybridisation of compressed gas and solid hydride storage tanks [43].

It is unlikely that the Li-ion batteries will attain a specific energy of 666 Wh kg^{-1}, as the optimisation of current chemistries has reached practical limits [8]. Several alternative chemistries are under development which could reach this goal in time, with lithium metal, lithium–sulphur, lithium–air and non-lithium

Table 5
Comparison of petrol, hydrogen and electrical storage systems in four leading vehicles.

	Conventional	Hybrid	Hydrogen	Battery
Reference vehicle	Volkswagen Golf VI	Toyota Prius III	Honda FCX Clarity	Nissan Leaf
Fuel weight (kg)	40.8	33.3	4.1	171[a]
Storage capacity (kWh)	500	409	137	24
Specific energy (Wh primary/kg fuel)	12,264	12,264	33,320	140[a]
Storage system weight (kg)	48	40	93	300[b]
Specific energy (Wh primary/kg of storage)	10,408	10,261	1,469	80
Net power (kW)	90	100	100	80
Power plant and auxiliary weight (kg)	233	253	222	100
Specific energy (Wh primary/kg total equipment)	1,782	1,398	315	60
Average conversion efficiency	21%	35%	60%	92%
Effective storage capacity (kWh usable)	105.0	143.1	82.0	22.1
Specific energy (Wh usable/kg total equipment)	374	489	260	55

[a] Bare laminated lithium-ion cells.
[b] Including battery management and cooling systems.

Table 6
Typical well-to-tank, tank-to-wheel and well-to-wheel efficiencies for each vehicle technology.

Vehicle type	Well to tank	Tank to wheel					Well to wheel
BEV	32–100%	Charger 90%	Battery 92%	Inverter 96%	Motor 91%	Mechanical 92%	21.3–66.5%
H$_2$ FCEV	75–100%	Fuel Cell 51.8%		Inverter 96%	Motor 91%	Mechanical 92%	31.2–41.6%
Hybrid	82.2%	30.2%					24.8%
Diesel	88.6%	17.8%					15.8%
Petrol	82.2%	15.1%					12.4%

intercalation chemistries all offering the potential of systems-level specific energies of at least 500 Wh kg^{-1} [44].

There are no near- or long-term developments in capacitor technology that are expected to deliver such an improvement in specific energy. Novel graphene electrodes have demonstrated specific energies up to 86 Wh/kg of bare electrode, implying around 20 Wh kg^{-1}for a complete system [45]. These developments are likely to spill over into battery electrodes, with graphene anodes offering the potential to double energy density in lithium-ion batteries [46].

4.4. Efficiency

A high charge/discharge or conversion efficiency is also important as it impacts on the overall energy efficiency, running costs and life-cycle CO$_2$ emissions of the vehicle. Maximising efficiency must be done at the expense of other goals, notably power density and charge/discharge rates, which in turn impact on system size, weight and cost.

Capacitors currently hold the advantage, with cycle efficiencies in the range of 90–98%, leaving little room for improvement.

Battery efficiency has also improved substantially with the transition from lead acid (75–85%) and NiMH (65–85%) to lithium chemistries. Under ideal conditions, cycle efficiencies of lithium-ion batteries now rival those of capacitors at 90–94% in automotive use [47–49].

Battery system efficiency is closely related to operating conditions, decreasing with both current and temperature. The desire of consumers to move to rapid charging systems is therefore cause for concern. When charged with a 3 kW household charger the charging efficiency of the Mitsubishi i-MiEV is around 90%; however, the 50 kW quick-charge option can be as little as 60% efficient, due to the additional energy required to cool the battery [47]. Inductive charging is another promising option, due to its speed and inherent safety; however, it reduces efficiency by a further 10% [50].

The US Department of Energy (DoE) and Japan's NEDO hydrogen energy roadmap both set a target of 60% efficiency for FCEVs circa 2015. It appears from the latest field trials in California that this target is close to being attained, with fuel cell vehicles from five major manufacturers averaging 52%, and the top manufacturer achieving 57% [41].

A vehicle's well-to-wheel (WTW) pathway traces from the original energy source through conversion, distribution and storage, to the wheels of the car. Table 6 summarises the typical well-to-tank (WTT) and WTW efficiencies for conventional and electrochemical vehicles.

The efficiency of these electrochemical systems only plays a part in determining the amount of energy required by the vehicle, and thus its fuel economy and maximum driving range. The energy required to move a vehicle scales linearly with its mass [51,52], and so doubling the vehicle's efficiency will have a negligible impact if its weight also doubles. This is clearly evident with the range of FCEVs produced to date. Despite 40 years of technical development, the Honda FCX Clarity has virtually the same fuel economy as the Austin A40 converted to run on an AFC developed by Professor Karl Kordesch in the 1970s [53]. Fig. 10 compares these vehicles with
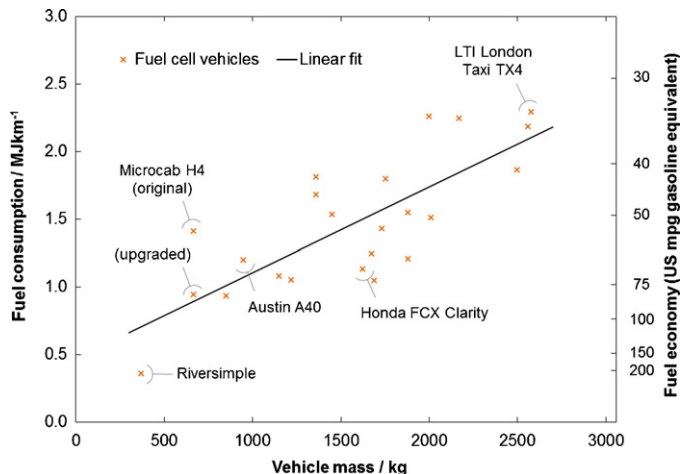
Fig. 10. Energy consumption (MJ km^{-1}) measured from 'real-world' testing of 23 hydrogen fuel cell vehicles, plotted against vehicle mass (kg) [51].

15 other models, demonstrating the relationship between mass and fuel economy.

4.5. Safety

Public and media-driven concerns about safety continue to dog the proliferation of hydrogen and battery powered vehicles, even though the technologies themselves are inherently and passively safe. Hydrogen cylinders are tested against crushing, impact damage, penetration with armour piercing bullets and fire [54]. Dr. Swain's infamous video experiment also demonstrated that a ruptured hydrogen tank would produce a more manageable and less destructive fire than a ruptured petrol tank [55].

Similarly, the majority of BEV manufacturers have avoided the use of lithium–cobalt, lithium–manganese and other unstable chemistries. The majority now use lithium iron phosphate, and so the battery packs in today's vehicles cannot experience thermal runaway. Coupled with well-specified cooling systems, precise monitoring of the pack's SoC and individual cell balancing, these should give a robust and fail-safe system [56].

5. Conclusions

There has been a lot of progress in electrochemical storage devices during the past decade, and the near future holds prospects for many further advances. Cost, durability and energy density are the main areas where improvements are required to compete with conventional fossil fuels.

Costs have been falling exceptionally rapidly, and are expected to continue doing so for the next 5–10 years. For example, the cost of manufacturing FCEVs has decreased by a staggering 90% since 2005, and the publicly acceptable goal of $50,000 for a luxury sedan is now within reach. BEVs have already reached such a price-point – with current vehicles retailing at around $40,000 – with $20,000–30,000 attainable within 10 years.

The durability of battery and capacitor technologies is already expected to be sufficient for automotive use, giving 10 years calendar life and 150,000 miles. Fuel cell stacks appear to still be falling short of the US DoE's 2009 target of 2000 h operation, corresponding to approximately 25,000 miles before a 10% drop in power output. New MEA designs with improved catalysts and reduced crossover currents are expected to improve this situation in the future.

Energy density is still the *Achilles heel* of batteries and capacitor technologies. It is a sad fact that even the latest nanotechnology-based ultracapacitors are not expected to offer close to the energy density of battery technologies, and so they are unlikely to ever be used for more than peak power provision. However, the high efficiency and relatively light ancillary systems required by electric power-trains mean that batteries need only offer 666 Wh kg^{-1} at the cell level to offer the same driving range and consumer acceptability as current petrol vehicles. The next generation of lithium-based chemistries are expected to approach this value, and so the perennial problem of 'range anxiety' may soon be overcome. Hydrogen storage will however be the first technology to exceed petrol in terms of the range offered, as only 6 wt.% hydrogen is required, and several forms of metal-hydride storage are on the horizon which are expected to beat this.

Recently, Japanese automakers announced at the 2010 Fuel Cell Expo in Tokyo a programme designed to deploy 2 million FCEVs in Japan by 2025, at which point the industry estimates FCEVs would be fully competitive. It has also become apparent that several (but not all) OEMs had redeployed their technical staff from fuel cell R&D to focus on Li-ion batteries. In addition, some of these automotive companies also stated that technology investment in the fuel cell supply chain is in serious decline. Thus, these two factors combined reduce the likelihood of the very fast progress in a hydrogen economy that was expected a few years ago. It is unlikely that global market forces alone will be able to achieve the IPCC 80% carbon reduction goal by 2050, the policy makers are therefore required to give an aggressive push towards this objective.

Acknowledgements

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