

A journey on the electrochemical road to sustainability

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Abstract As the nations of the world continue to develop, their industrialization and growing populations will require increasing amounts of energy. Yet, global energy consumption, even at present levels, has already given rise to major concerns over the security of future supplies, together with the attendant twin problems of environmental degradation and climate change. Accordingly, countries are examining a whole range of new policies and technology issues to make their energy futures ‘sustainable’, that is, to maintain economic growth and cultural values whilst providing energy security and environmental protection. A step in the right direction is to place electrochemical power sources—serviceable, efficient and clean technology—at the cutting edge of energy strategies, regardless of the relatively low price of such traditional fuels as coal, mineral oil and natural gas. Following a chronicle of the events that led up to the discovery of batteries and fuel cells, the paper discusses the application of these devices as important technology for shifting primary

energy demand away from fossil fuels and towards renewable sources that are more abundant, less expensive and/or more environmentally benign. Finally, consideration is given to the idea of introducing hydrogen as the universal vector for conveying renewable forms of energy and also as the ultimate non-polluting fuel. Fuel cells are the key enabling technology for a hydrogen economy. As requested, the paper opens with a brief account of the circumstances by which the author joined others on a fascinating journey on the electrochemical road to sustainability.

Keywords Battery · Electricity · Electric vehicle · Electrochemistry · Fuel cell · Hydrogen · Renewable energy · Sustainability

Many are called, but few are chosen

Although neuroscientists from the Duke University Medical Center claim that older people are able to look back at the world through rose-tinted spectacles [1], it is my firm belief that I grew up in the best of times, in the best of places—to paraphrase Charles Dickens, whose birthplace was but a short distance from my family home.

My education started in the late 1940s at Purbrook Infant School in Hampshire, England. At that time, the new Labour government was attempting to revitalize Britain through finding ways to tackle want, disease, ignorance, squalor and idleness—the five ‘giant’ problems that had been highlighted earlier in the 1942 Beveridge Report. This document had argued that remedies would be found through the government providing adequate income to people, adequate health care, adequate education, adequate housing and adequate employment. The resulting aggressive legislation saw the nationalization of the power industries (coal, gas, electricity), the steel

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industry, the railway and road haulage networks, ports and civil aviation, and the health care and insurance systems. The overall aim was nothing less than full employment throughout the country with the most basic needs to be administered by the government, in essence, the construction of a ‘Welfare State’. Previously, the Butler Education Act of 1944 had introduced a tripartite system that made secondary education free for all pupils in grammar schools, secondary technical schools or secondary modern schools. It also created a system of direct grant schools, under which certain independent schools received a direct grant from the Ministry of Education in exchange for allocating ‘free places’ to a number of pupils. Under the benefits provided by the Welfare State and the Butler Education Act, we grew into the healthiest and most widely educated of generations.

The early 1950s saw the long period of privation associated with rationing draw to a welcome close. All rationing came to an end in 1954—the year that my secondary education commenced at Portsmouth Grammar

School, a direct grant institution. The lifting of restrictions on paper supplies encouraged publishers of comic and other magazines to increase their content and bring out many new titles. We avidly read the *Eagle* in which Dan Dare, Pilot of the Future, fought supersonic battles with the Mekon, the super-intelligent ruler of the Treens of northern Venus (Fig. 1). Meanwhile, the *Lion* featured the adventures of Captain Condor, who was a space pilot from the year 3000 and had been banished to an uncharted moon called Zor. Each week, with millions of other listeners, we tuned into the BBC Light Programme to join Jet, Lemmy, Doc and Mitch in the next thrilling installment of *Journey Into Space*, and were horrified by the alien beings that threatened to destroy humanity in BBC Television’s serialization of the *Quatermass* trilogy (Fig. 1). Such fictitious escapades moved a step closer to credibility when Soviet scientists managed to put a sizeable satellite into orbit in 1957 (Sputnik I, powered by a silver–zinc battery). In response, the USA accelerated its research activities in a



Fig. 1 BBC serials and comic magazines of the 1950s—popularization of science, particularly for impressionable young minds

major effort to catch up with the Russians. Thus, the ‘race for space’ had begun, particularly with respect to being the first to the moon—an achievement deemed by both countries to be essential for national security and to be symbolic of technological and ideological superiority. Elsewhere, *Nautilus*, a nuclear-powered submarine with an auxiliary battery of 126 lead–acid cells, had moved beneath the North Pole, and I well remember the South Parade Pier in Southsea (where I had taken a ‘summer holiday’ job) shuddering as the 4-tonne Saunders-Roe SR-N1 hovercraft passed by en route for the Isle of Wight.

Indeed a host of discoveries and inventions were changing the everyday world around us. For instance, the decade saw the introduction of mass-produced computers, colour television, cinemascope, heart-pacemakers, a huge variety of plastic goods, commercial jet services, transistor hearing aids, transistor radios, nuclear power plants, fibre optics, solar-powered hot water systems, videotape recorders, portable electric typewriters, non-stick frying pans and electronic synthesizers. In other fields of endeavour, Jonas Salk had developed a polio vaccine, and Francis Crick and James Watson had elucidated the structure of deoxyribonucleic acid.

Clearly, during the 1950s, people were turning to scientists and technologists to solve their problems more often than ever before. No wonder then that it became a widely held view that a career in science, whatever the discipline, would lead to gainful employment. Consequently, in my final years at school, I was ‘encouraged’ to forsake geography, history and Latin (three of my pet subjects), to dispel all thoughts of becoming an archaeologist, and to concentrate on chemistry, pure and applied mathematics and physics. To be truthful, little persuasion was needed in the case of chemistry. My uncle had given me a chemistry set to conduct experiments at home and, in those days, the most amazing chemicals could be readily bought over the counter; with these I even made my own fireworks, though not always successfully. The school’s laboratories were very well equipped and there were no draconian occupational health and safety procedures to dampen a student’s curiosity. Through this empowerment, it is likely that we reached a greater level of responsibility in the handling of chemicals than that achieved by students today. I do not recall any serious accidents.

There were also school outings to scientific meetings and my nascent ambition to become a research scientist was strengthened after listening to a mesmerizing account of the wonders of inorganic chemistry by Professor Ronald Nyholm; I have in mind that this was part of the Science Teaching project established by the Nuffield Foundation. We were further blessed by having an exceptionally gifted group of schoolmasters. They were mostly Oxbridge graduates and naturally we were educated to follow in their footsteps. In due course, I informed the head

chemistry master of my intention to apply to Cambridge, his alma mater. “Well, Rand,” he said, “you must remember that many are called, but few are chosen!” With this note of caution still running through my head, a few weeks later on a cold and foggy December morning, I found myself in the company of a feverish mass of other young hopefuls outside the Cambridge Corn Exchange. We were awaiting the start of the university admission and scholarship examinations.

I have little recollection of those Cambridge examinations, except for the extremely stressful 24 hours during which candidates waited to hear whether they had passed the written papers and thereby would be invited to proceed to the ‘practicals’. It was exciting to learn that the physics practical—to determine the optical efficiency of a light bulb—was to be conducted in the famous basement of the Cavendish Laboratory. Whereas this room was doubtless the Mecca for the aspiring physicists amongst us, I found it to be a damp and depressing place. My spirits were lifted the next day, however, by the more modern Chemistry Laboratories, and I set about identifying the ‘unknown substance’ with gusto. Two weeks later, whilst sorting Christmas mail (another holiday job) at the General Post Office in Portsmouth, the worker on the next table handed me a telegram. It bore my name and had a Cambridge postmark. The brief message informed me I was among ‘the few that had been chosen’.

I went up to Trinity Hall in October 1961 and enrolled for the Natural Sciences Tripos. Part I of this course required students to take three experimental subjects. So, in my second year, in addition to continuing with chemistry and physics, I elected to take biochemistry. It was the autumn of 1962. The Laboratory of Molecular Biology had been opened earlier that year by Queen Elizabeth II to consolidate and expand the research of Francis Crick and James Watson (share of the Nobel prize for physiology or medicine, 1953), Frederick Sanger (Nobel prize for chemistry, 1958; share of the same prize, 1980), John Kendrew and Max Perutz (Nobel prize for chemistry, 1962) and Sydney Brenner (share of the Nobel prize for physiology or medicine, 2002). Not surprisingly, with such a galaxy of lecturers, biochemistry was an extremely popular subject. It was essential to arrive at least an hour before a lecture and, even then, there was every possibility of being greeted by a ‘house full’ notice, even at 8 am on a Saturday morning. To compound the problem, many academic scientists from diverse faculties were equally enthusiastic attendees, especially when Crick was the presenter—he was quite a showman! Given the extreme popularity of the subject and the fact that I had little fundamental knowledge of biological processes, I quickly relinquished all aspirations of becoming a molecular biologist. Instead I decided to major in organic chemistry as I also held a fascination for

the design and synthesis of new molecules, particularly those with potentially useful properties.

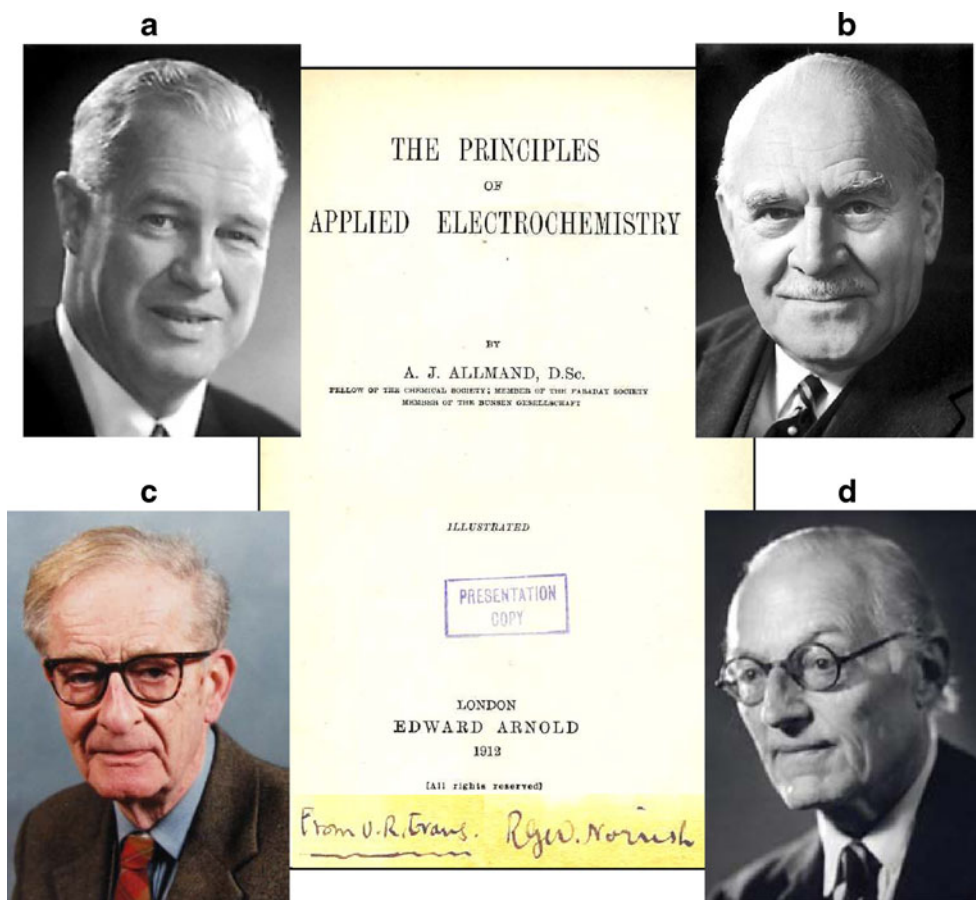
Just before the Part II examinations and still attracted to certain aspects of biochemistry, I had the temerity to seek an interview with Lord Todd (Nobel prize for chemistry, 1957) with the prospect of conducting post-graduate research on nucleotides (Fig. 2a). It was an unnerving experience. I entered a room that surely was more befitting a stately home than a chemistry laboratory. Lord Todd, a tall man, was reclining so far back in his chair that I was obliged to converse throughout with the soles of a pair of shoes which rested atop the highly polished desk. I have no memory of what passed between us except for my interrogator's final words, delivered in a strong Scottish brogue: "Remember, laddie, many are called, but few are chosen!" Was history to repeat itself? This seemed very unlikely when the examination results were published and, a few days later, I was not among the happy few who were summoned to the Department of Organic Chemistry to become 'Toddlers'.

Without any long-term plans, I joined the Unilever Research Laboratory at Vlaardingen in The Netherlands to undertake a 6-week 'work experience' project. The research was aimed at understanding the mechanism of fat bloom formation in dark chocolate. On 24 July 1964, whilst

investigating phase transitions in molten chocolate by means of a rotating viscometer (and listening to Cowper reach 311 during the 4th Test Match between England and Australia at Old Trafford, Manchester), I received a telephone call from Dr. J N Agar in Cambridge (Fig. 2c). "Would you like to become an electrochemist and do you know anything about fuel cells?"— he enquired.

John Agar completed his Ph.D. in the Laboratory of Physical Chemistry, Cambridge, in 1938 under the supervision of F P Bowden FRS—the same year that their seminal paper, 'The Kinetics of Electrode Reactions. I and II', was published in the *Proceedings of the Royal Society* [2]. The paper was communicated by R G W Norrish FRS (Fig. 2b), and reference to the work has continued to this day; its importance is discussed below. John then moved to the neighbouring Corrosion Laboratory to serve as a research assistant to U R Evans FRS, who was later described in the Biographical Memoirs of the Fellows of the Royal Society as the 'Father of the modern science of corrosion and protection of metals'. After being involved in a number of projects that tackled corrosion problems in ships, John returned to the Laboratory of Physical Chemistry in 1945. John died on 11 July 1996 and the following two extracts from an obituary [3] written by Robin Turner, a former research student, paint a consummate portrait of this gifted

Fig. 2 **a** Sir Alexander Robertus Todd, Baron Todd of Trumpington (1907–1997), **b** Ronald George Wreyford Norrish (1897–1978), **c** John Newton Agar (1914–1996), **d** Francis Thomas Bacon (1904–1992)



scientist, who would puff on his pipe, scribble a few equations (always in pencil) and quickly offer an ingenious solution or comment with a shy smile.

‘He was the gentlest of men, but carried an aura of scholarship which a subsequent colleague of mine, now a Reader himself, described as ‘frightening’. Both of us found him anything but frightening if you talked to him. [...] His office was lined with notebooks dealing with all sorts of topics which had caught his attention. He lent them to me from time to time, and it was a struggle to keep pace with both the science and the handwriting.’

‘He was a most unassuming man who always seemed to wear the same tweed jacket. He had the least inflammable pipe I have ever known—it consumed more matches than tobacco, and its knocking out on the central heating pipe in his office told everyone else that he was in. He drove a small open-top car of similar vintage to his pipe and jacket and was the least materialistic of men. He could be very funny, in a kind way, about the modern trends in academia, which were certainly not to his liking.’

My research was directed towards an elucidation of the complex behaviour of porous gas diffusion electrodes in fuel cells. I was extremely fortunate to be engaged in such work given the fact that space exploration was then in full swing and these power sources were key technology for spacecraft. There were also visits from John Agar’s friend, Francis Thomas (‘Tom’) Bacon (Fig. 2d), who had built a practical alkaline fuel cell at Marshall of Cambridge Limited (1956–1961). His circulating electrolyte design was taken up in the USA by the Pratt and Whitney Aircraft Company (later the United Technologies Corporation) and was used by the National Aeronautics and Space Administration in all 18 of its Project Apollo missions, v.i. Tom Bacon was always extremely gracious and gave freely of his time, even to novice electrochemists. It was easy to see why he and John Agar were good friends. In later years, I considered it to be a privilege to meet and correspond with him.

The research students in the now-called Department of Physical Chemistry enjoyed a great camaraderie, both among themselves and with the academic staff. The electrochemists were in a distinct minority as most activity was devoted to wide-ranging research on the kinetics of photochemical gas phase reactions, especially with respect to short-lived transient species, by means of flash photolysis. This technique had been developed by Professor Norrish, the Head of Department, in collaboration with G H Porter FRS, and by M Eigen in Germany; in 1967, all three shared the Nobel Prize in Chemistry for its invention. Norrish occupied the chair until 1965 when he retired as Emeritus Professor of

Physical Chemistry in the university. He moved into an office immediately across the small corridor from my own laboratory and often enquired about the progress of my research. One day, he thrust a copy of A J Allmand’s *The Principles of Applied Electrochemistry* [4] into my hands: “Read and learn, dear boy, read and learn” he said and then suggested that we might wander down to the Spread Eagle for a snifter (over the years, many lively chemistry gatherings were held in that atmospheric hostelry). Remarkably, Allmand’s book had been presented to him by U R Evans (Fig. 2). Were the hidden forces that shape our destiny directing me towards a long-term commitment to electrochemistry?

J E B Randles, the eminent electrochemist who had made important contributions to the theory of cyclic voltammetry and electrochemical impedance spectroscopy, was appointed as the external examiner of my thesis. It was a frightening prospect to be quizzed by him and Agar in tandem. I scrutinized the University Statutes and Ordinances and found that it was mandatory for me to wear the hood and gown of the Bachelor of Arts degree, but it was unclear whether an academic cap (‘mortarboard’) was obligatory. I decided to err on the side of caution, much to the great amusement of my interrogators who immediately awarded me ten bonus points for being the first fully dressed Ph.D. candidate within living memory to be seen in the chemistry laboratories. In retrospect, these amiable scientists were, of course, putting me at my ease. And so the dye was cast—I now realized that I was indeed to pursue a career in electrochemical science.

Whilst spending his sabbatical leave at the University of New England, Australia, with his former Ph.D. student R A Stokes (co-author of the definitive book *Electrolyte Solutions* [5]), John Agar had taken the opportunity to travel to Melbourne and visit the electrochemistry group of the Commonwealth Scientific and Industrial Research Organisation (CSIRO)—Australia’s national science agency. He judged their research expertise and facilities to be ‘quite impressive’ (John was not given to the use of superlatives), and since they were looking for an electrochemist to conduct research into improved electrocatalysts for fuel cells, he suggested that I might apply for the position. Two months later, my wife and I embarked on a 31-day voyage to Melbourne. We migrated as ‘Ten Pound Poms’ under the Assisted Passage Scheme that had been established by the Government of Australia to increase the population and to supply workers for the country’s burgeoning industries. (By way of interest, the current Prime Minister of Australia, Julia Gillard, had migrated from Wales with her family 3 years earlier but, as a child, she was allowed to travel for free.) On a wet and windy Monday morning, I entered the CSIRO Division of Mineral Chemistry to find the entire staff gathered around an extremely small and venerable black-and-white television set. Unwittingly, I had timed my arrival almost to the minute that Neil Armstrong had set his left boot

on the surface of the moon (2:56 Coordinated Universal Time, 21 July 1969). Immediately, my thoughts turned to Tom Bacon, whose pioneering work on fuel cells had enabled Apollo 11 to undertake this epic journey into space.

The CSIRO research group was led by David Koch and included the notable scientists Tom Biegler, Keith Cathro and Ron Woods. These were the halcyon days of electrochemistry in Australia—a time made more remarkable by the arrival of John O'M Bockris at Flinders University in 1972. A particular highlight was the establishment of the biennial Australian Electrochemistry Conference by the Electrochemistry Division of the Royal Australian Chemical Institute. The meetings (which have continued to this day) readily attracted a galaxy of distinguished speakers from all parts of the world and featured the presentation of the Breyer Medal for internationally recognized contributions in the field of electrochemistry. This award commemorates the life and work of Bruno Breyer, who was born in Czechoslovakia, educated in Germany, and later in Australia became a pioneer of alternating current polarography. Past recipients have included G J Hills, J O'M Bockris, F T Bacon, R Parsons, A J Bard, M Fleischmann, H Gerischer, H A O Hill, R W Murray, F C Walsh, A G MacDiarmid, J-M Savéant and R G Compton. As there seemed little advantage to be gained by leaving this scientific nirvana, I accepted a permanent position at CSIRO and proceeded to undertake a succession of studies on direct methanol fuel cells, the electrochemistry of sulfide ore flotation, secondary batteries and hydrogen energy.

It is my firm belief that electrochemistry, a truly interfacing science, is vital to the future well-being of the planet. My reasoning is as follows. The primary sources on which we depend for our energy are not always of a form that is suitable for the intended end-use. Instead, the sources may have to undergo a single- or multiple-step conversion process. The most important, versatile and useful of these 'secondary' energy sources is electricity. Electrical energy can be obtained and stored by means of electrochemical reactions in devices that may play increasingly important roles in future strategies to improve the efficiency of energy supplies, as well as to shift the demand for primary energy away from fossil fuels towards sources that are more abundant and more benign, i.e. so-called renewable energy. To justify the assertion that research in the field of electrochemistry is integral to the successful attainment of global energy sustainability, the following is an evaluation of the past, present and future of this science.

Unravelling the mysteries of electricity

The name 'electricity' was coined by William Gilbert, physician to Queen Elizabeth I of England and Ireland (Fig. 3a). The publication of his book *De Magnete* in 1600

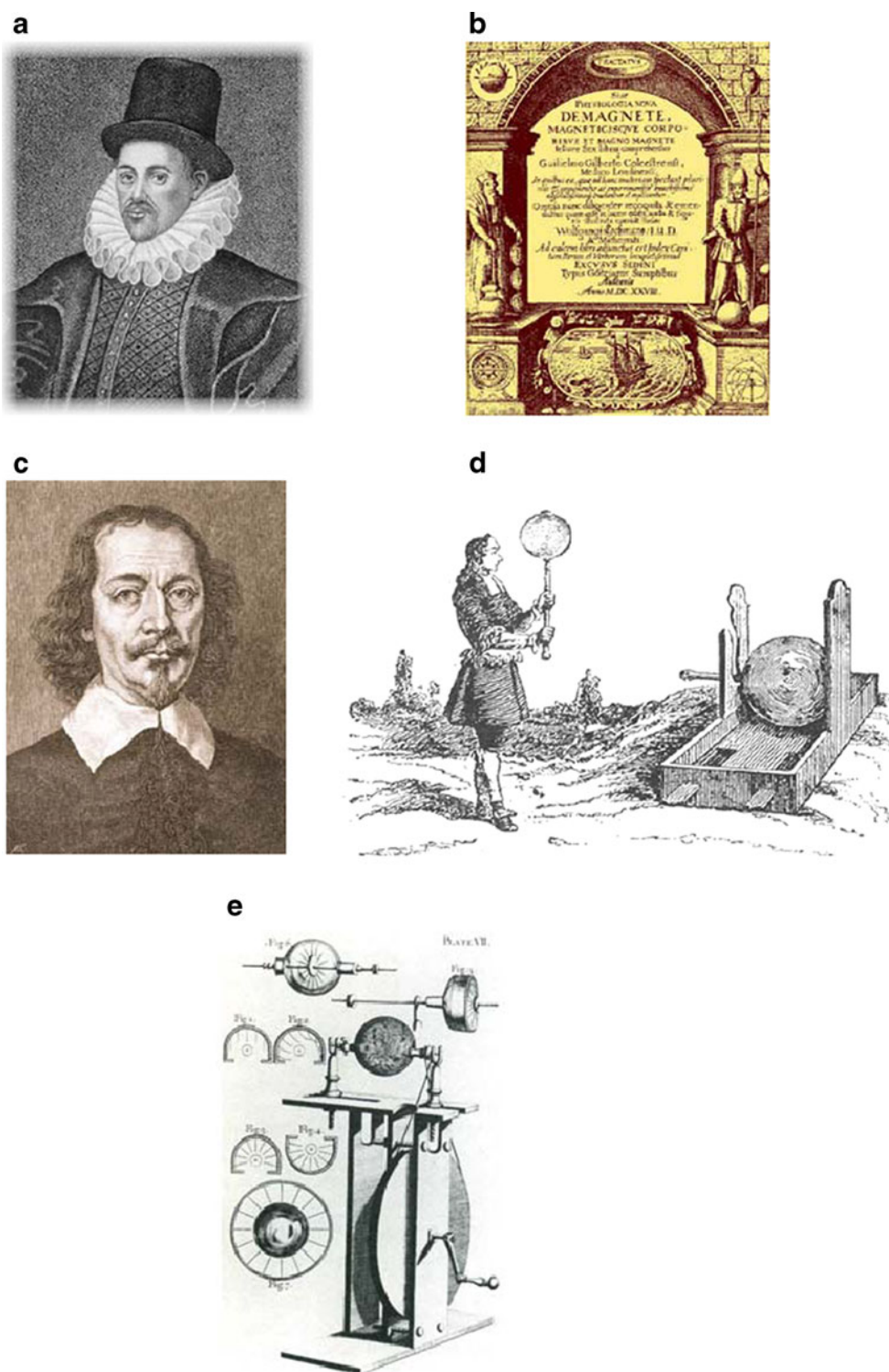
marked the beginning of the scientific understanding of magnetic and electrical phenomena (Fig. 3b). In particular, the work included details of the creation of static charge by rubbing amber and other materials with a piece of cloth or fur. It should be noted that, although none of his own writings survived, Thales of Miletus (c. 625–547 BC) had probably performed similar experiments with amber in Ancient Greece. In fact, the word 'electricity' comes from 'elektron', the Greek name for amber. Gilbert invented possibly the earliest electrical instrument, the 'versorium', which was simply a metal needle allowed to pivot freely on a pedestal, i.e. like a compass. With this device, he tested many materials that had been charged by friction and then classified them as 'electrics' or 'non-electrics' according to whether or not they attracted the needle. In other studies, Gilbert explained why suspended lengths of magnetized iron automatically aligned in a north–south direction by likening the Earth to a large magnet. The versorium needle responded identically regardless of whether the materials developed attractive or repulsive forces when rubbed, unlike a compass needle which is magnetized and can therefore distinguish between the 'north' and 'south' poles of a magnet. Thus, Gilbert was the first to draw a clear distinction between static electricity and magnetism.

In the 1660s, Otto von Guericke, a German scientist/inventor and also the mayor of Magdeburg, built a 'friction machine' to generate electrical charge (Fig. 3c, d). This consisted of a ball of sulfur that was cast on an axle which was turned by a winch. Whilst being rotated rapidly by the investigator, the ball was rubbed by an assistant with the palms of the hands and the resulting friction induced a strong electric charge on the sulfur. The sphere was then lifted by its spindle and carried to where electric experiments were to be performed.

Francis Hauksbee (also known as Francis Hawksbee), an assistant to Sir Isaac Newton and a demonstrator of experiments at the Royal Society, found that practical amounts of charge could be obtained by replacing von Guericke's sulfur ball with a glass globe (Fig. 3e). In one experiment, he placed a small amount of mercury in the glass, evacuated the air and built up a charge on the ball. When touched on the outside, the ball shone with a purple blue-green glow and lines of light crackled like lightning within. In 1709, Hauksbee published *Physio-Mechanical Experiments on Various Subjects. Containing an Account of Several Surprising Phenomena Touching Light and Electricity*. This book gave rise to a proliferation of electrical demonstrations in which large sparks were generated to the amazement of audiences in lecture halls, spectators at public shows and guests invited to private parties.

Stephen Gray, a former cloth dyer, devised techniques for transmitting charge along very long lengths of thread and wire (Fig. 4a). From the results of experiments

Fig. 3 **a** William Gilbert (1544–1603), **b** Title page of second edition of Gilbert’s *De Magnete* (1628), **c** Otto von Guericke (1602–1686), **d** von Guericke’s sulfur electrical machine (1660s), **e** Hauksbee’s glass electrical machine (1719)

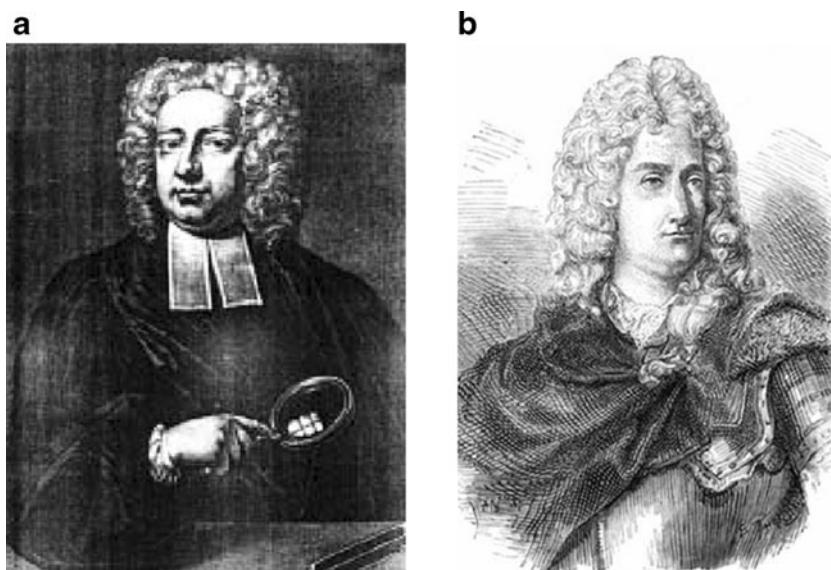


performed between 1729 and 1726, Gray proposed that any object on touching an electrically charged body will itself become electrified. Gray referred to the phenomenon as ‘electrical communication’ and identified different materials that fell into the categories of those that would convey electricity and those that would not. In 1736, the Frenchman Charles Du Fay (Fig. 4b) conceived a model of

electricity that described the phenomenon in terms of two different fluids. He proposed that [6]:

[...] there are two distinct electricities, very different from one other; one of which I call vitreous electricity, and the other, resinous electricity. The first is that of glass, rock-crystal, precious stones, hair of

Fig. 4 **a** Stephen Gray (1666–1736), **b** Charles François de Cisternay Du Fay (1698–1739)



animals, wool, and many other bodies; the second is that of amber, copal, gum-lack, silk, thread and a vast number of other substances. The characteristic of these two electricities is that a body of vitreous electricity, for example, repels all such as are of the same electricity; and on the contrary, attracts all those of the resinous electricity’.

Du Fay was well aware of Gray’s work and suggested that the best material for a transmission line should be a non-electric or a ‘conductor’, whereas the supports for the line should be made from an electric or an ‘insulator’. Accordingly, these two terms entered the scientific vocabulary.

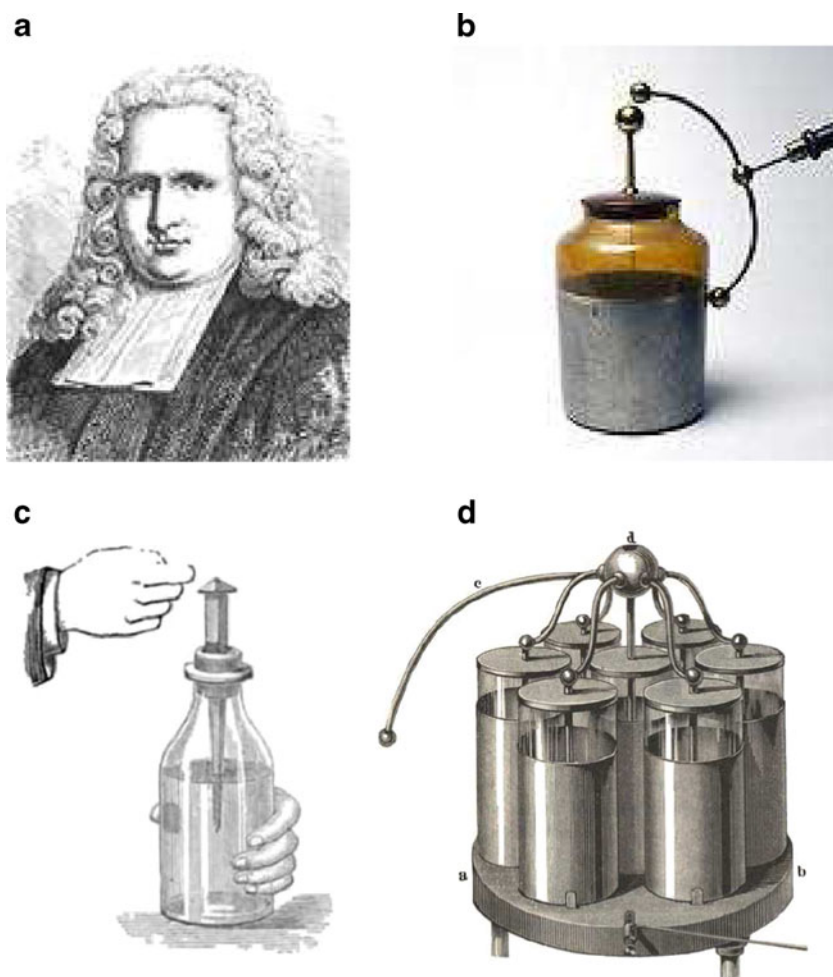
A device that could store large quantities of static electricity was invented independently by the German cleric Ewald Georg von Kleist on 11 October 1744 and by the Dutch scientist Pieter van Musschenbroek of Leyden in 1745–1746 (Fig. 5a). Following a period of experimentation, the so-called Leyden jar was perfected and the eventual design consisted of a glass jar with outer and inner metal coatings (typically, silver or tin foil) that covered the bottom and sides nearly to the neck (Fig. 5b). A brass rod, which terminated in an external knob, passed through a wooden stopper at the top of the jar and was connected to the inner coating by a loose chain. On applying an electrical charge to the external knob from a friction machine, charges accumulated on the two metal coatings (or ‘plates’), but they were unable to discharge due to the intervening layer of glass. Thus, the charges held each other in equilibrium until a discharge path was provided, such as that shown in Fig. 5b. In essence, the device was an early form of what is now called a ‘capacitor’. It should be noted that the original design was simply a glass jar with a metal nail. The latter passed through the stopper and made contact

with water, which partially filled the jar and acted as the inner plate. The role of the outer plate was taken by the hand of the experimenter. A charged jar could be discharged by approaching the nail with a finger, as shown in Fig. 5c. The charge from the water would jump via a spark to the hand and flow through the body to the other hand holding the jar. This often resulted in a nasty shock. It is not surprising, therefore, that Musschenbroek gave good warning of his ‘new but terrible experiment, which I advise you never try yourself’!

Soon, assemblies of several Leyden jars connected in series were being employed to furnish massive discharges [7] (Fig. 5d). For instance, in the spring of 1746, the Abbé Jean Antoine Nollet (Fig. 6a) electrified a row of 200 Carthusian monks in Paris. Each participant was joined to the next by a 25-ft length of iron wire. With some satisfaction (and probably amusement), the Abbé Nollet noted that all the monks started swearing, contorting or jumping in sharp response to a discharge from a Leyden jar which had been charged from a glass globe design of a generator (Fig. 6b). In a further demonstration in front of King Louis XV at Versailles, he sent a current through a chain of 180 Royal Guards. The King was highly amused when the soldiers all reacted simultaneously on completion of the circuit.

In October 1746, following a detailed series of experiments, the English apothecary and physician William Watson (Fig. 7a) communicated to the Royal Society his hypothesis that the electrified actions are due to the presence of an electrical ‘ether’, which in the charging or discharging of a Leyden jar is transferred but not created or destroyed [8]. Consequently, he proposed that the vitreous and resinous types of electricity postulated by Du Fay were, respectively, a surplus and a deficiency of a single fluid.

Fig. 5 **a** Pieter van Musschenbroek (1692–1761), **b** improved ‘two-plate’ Leyden jar, **c** sketch of earlier water-filled Leyden jar, **d** illustration of assembly of Leyden jars [7]



Meanwhile, the same theory had been independently developed by the American statesman–scientist Benjamin Franklin (Fig. 7b), and the two men became allies in refuting Du Fay’s two-fluid model of electricity in favour of a single-fluid version. In particular, Franklin assigned a positive sign ‘+’ for a gain in electricity and a negative sign ‘−’ for a loss of electricity. This, in turn, led him to the idea that charge is conserved, that is, electricity can be moved

around without loss and the overall amount of negative charge must balance the amount of positive charge. Arbitrarily (or for a reason that was not recorded), Franklin identified the term ‘positive’ with vitreous electricity and the term ‘negative’ with resinous electricity. The flow of electricity follows from this definition, but this causes some confusion now that it is understood that electricity is usually conveyed by the passage of negatively charged

Fig. 6 **a** Abbé Jean Antoine Nollet (1700–1770), **b** Nollet’s glass-globe electrical machine (an improved version of the von Guericke generator)

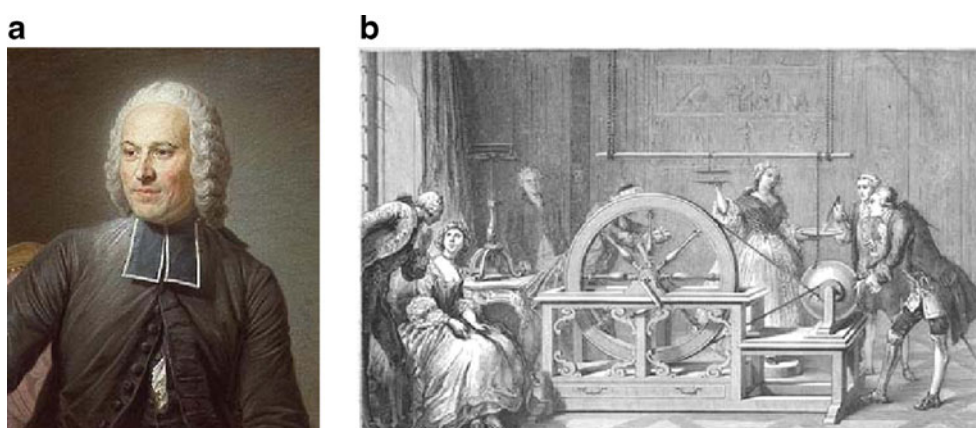
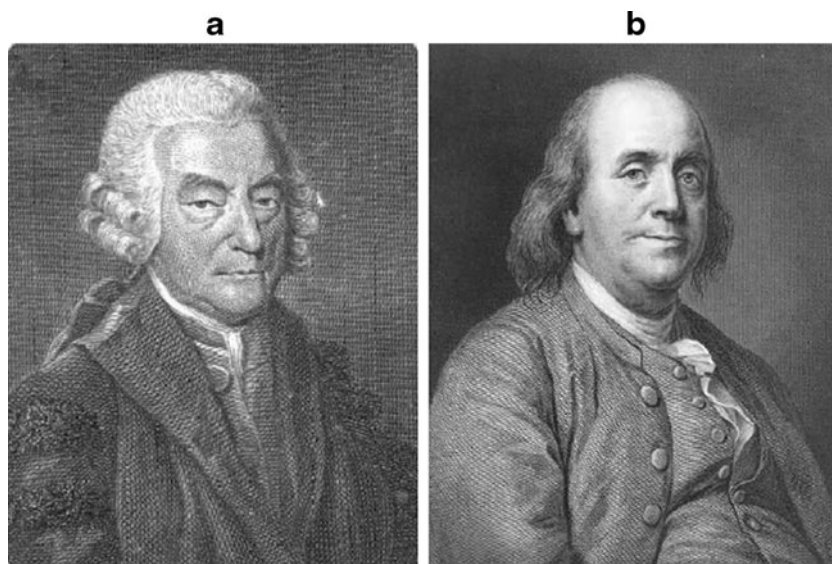


Fig. 7 **a** William Watson (1715–1787), **b** Benjamin Franklin (1706–1790)



particles. The final acceptance of the Watson–Franklin single-fluid theory came in the first half of the eighteenth century from research on phenomena discovered in vacuum tubes. It should also be noted that Franklin, through undertaking the extremely risky experiment of flying a kite in a thunderstorm, proved that lightning was an electrical phenomenon—by the fact that a metal key, placed on the ground and attached to the conductive string of the kite, became electrified.

The trail-blazing studies performed by the above scientists, and others, were not alone sufficient to guarantee and sustain universal interest in the still highly speculative field of electricity. Devices such as the Leyden jar or Benjamin Franklin's conductive kite strings discharged their electricity in a single blast that gave scientists few ways to experiment with the mysterious fluid. The situation was to change, however, following a remarkable and serendipitous discovery that was eventually reported towards the end of the eighteenth century.

Invention of the primary cell (battery)

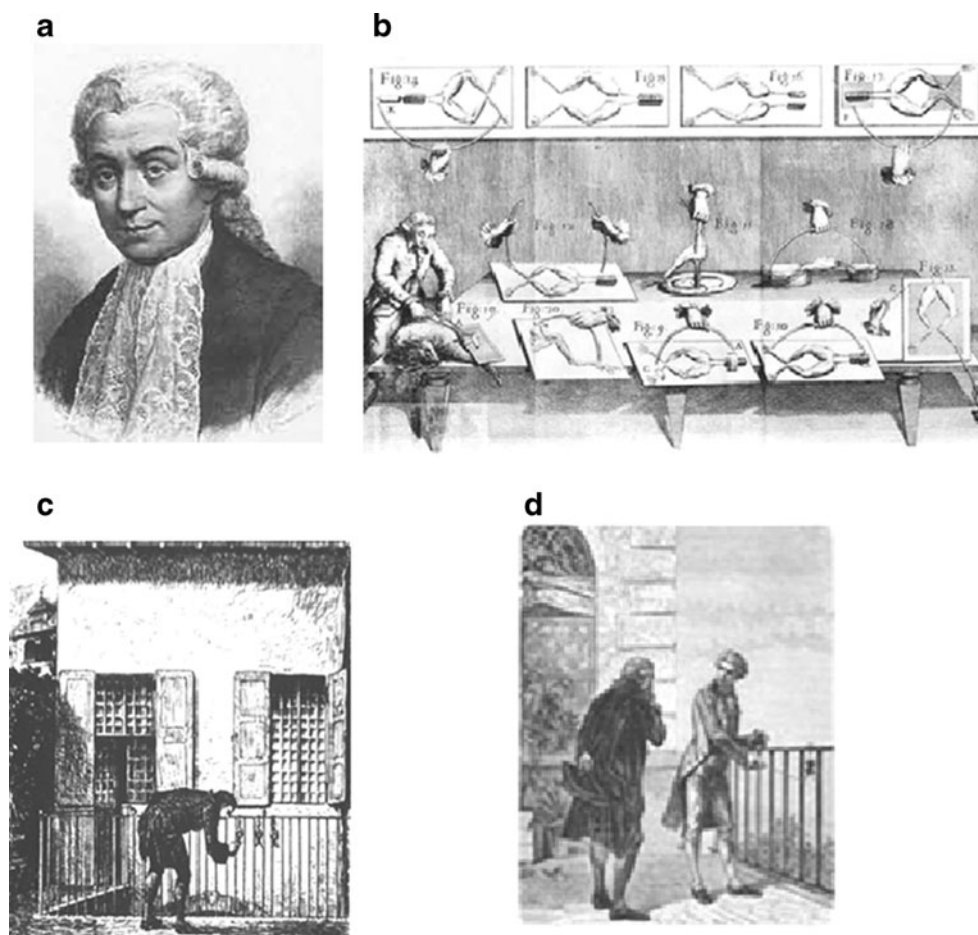
Colonel John Walsh, a member of the Parliament for Worcester and a fellow of the Royal Society, became fascinated by reports of the torpedo fish. In 1772, he travelled to La Rochelle in France to capture and study them. He concluded that their ability to deliver powerful electric shocks was akin to that of the Leyden jar.

Luigi Galvani, a lecturer in anatomy at the University of Bologna and a professor of obstetrics at the separate Institute of Arts and Sciences, began a series of experiments on frogs in the late 1770s to prove that animals did indeed possess 'intrinsic electricity' (Fig. 8a, b). Although these

studies may well have been inspired by the work of Colonel Walsh, Galvani declared that his interest in the subject had arisen from observing convulsions in the muscle of a frog laid out for dissection on a table where there was also an electrical machine. Galvani showed that this behaviour could be induced by connecting a dead frog directly to such a machine or if the frog were placed on a metal surface during a thunderstorm. The pivotal discovery, however, was made in September 1786 when he noticed that, on being hung out to dry on the fence outside his house, the frogs' legs twitched when the brass hooks used to suspend them came into contact with the iron railings (Fig. 8c, d). After repeating the experiment indoors, with no outside source of electricity, he decided that the legs were stimulated by electricity stored, or created, within the animal tissue itself. He further surmised that this electrical fluid was quite separate from both the 'artificial' static electricity produced by friction and the 'natural' electricity in lightning. Galvani delayed the announcement of his findings until 1791, when he published an essay entitled *De Viribus Electricitatis in Motu Musculari Commentarius* [9], but his advocacy for 'animal electricity' proved to be ill-founded.

Alessandro Volta, the professor of experimental physics at Pavia University, was among those who disagreed with Galvani's findings (Fig. 9a). He therefore proceeded to experiment with whole frogs and soon reached the conclusion that an electrical fluid flowed when two different, and physically connected, metals were applied to any conductive moist body. To demonstrate his idea, he constructed a pile of alternating discs of copper (or silver or brass) and zinc (or tin) that were separated by pasteboard discs (or 'any other spongy matter') soaked in brine (Fig. 9b). When the top and bottom of the pile were connected by a wire, the assembly delivered, for the first time in history, a more or less steady

Fig. 8 **a** Luigi Galvani (1737–1798), **b** Galvani's illustration of his experiments, **c, d** illustrations of Galvani hanging frogs' legs from the railings of his house



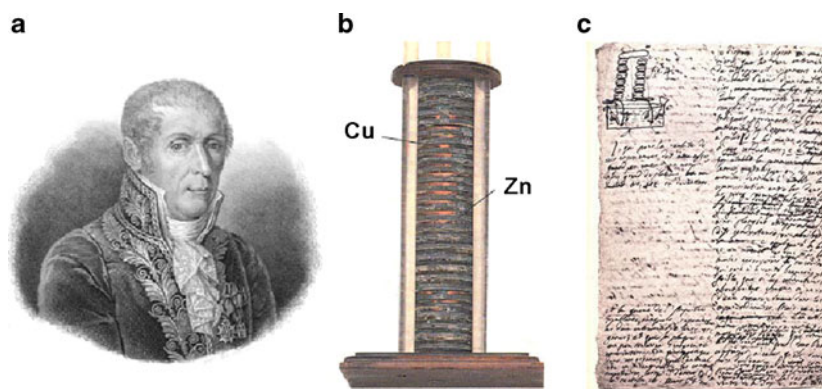
flow of electricity—unlike the Leyden jar which was an ‘all-or-nothing’ device that discharged its electricity in one action. Volta introduced the terms ‘electric current’ and ‘electromotive force’, the latter to denote the physical phenomenon that causes the current to flow. In due course, he conveyed his findings in a letter dated 20 March 1800 to Joseph Banks, the then President of the Royal Society (Fig. 9c). The communication was subsequently read to a meeting on 26 June 1800 but was not published until the September issue of *Philosophical Transactions* [10], as discussed below. Known as the ‘Volta (or Voltaic) pile’, this was the first ‘primary’ (or non-rechargeable) power source, as opposed to a ‘secondary’ (or rechargeable) power source, v.i.

Following the invention of the Volta pile, scientists were no longer restricted by the limitations of static electricity but could now work with electric currents that could be turned on and off at will. It was found that the current could be strengthened by adding more three-disc units (or ‘cells’) wired together in parallel or could be weakened by taking units away. Furthermore, the electromotive force was increased when two or more units were joined in series to form a ‘battery’—a term that had been introduced earlier by Franklin

to represent a storage unit composed of an assembly of Leyden jars, such as that shown in Fig. 5d, which he likened to a battery of cannon, i.e. cannons grouped into one place. Strictly speaking, a battery is a multi-cell array, although in common usage many single cells (particularly primary cells) are called ‘batteries’. In the following discussion, ‘battery’ is used to encompass both single cells and multi-cell devices housed in a single container.

Napoleon Bonaparte was so impressed by Volta's experiments that he persuaded the professor to visit Paris and demonstrate his invention to the members of the Institute of France. The Emperor himself helped with the experiments—he drew sparks from the pile, melted a steel wire, discharged an electric pistol and decomposed water into its elements. An overly enthusiastic Napoleon made Volta a member of the Institute, then a knight, and finally a count and a senator of the Kingdom of Lombardy. In addition, he awarded Volta a gold medal and provided him with financial assistance for many years. Remarkably, however, Volta published nothing on electrical subjects during the last 25 years of his life. In stark contrast, Galvani lost his position at the University of Bologna for refusing to swear allegiance to Napoleon's government in

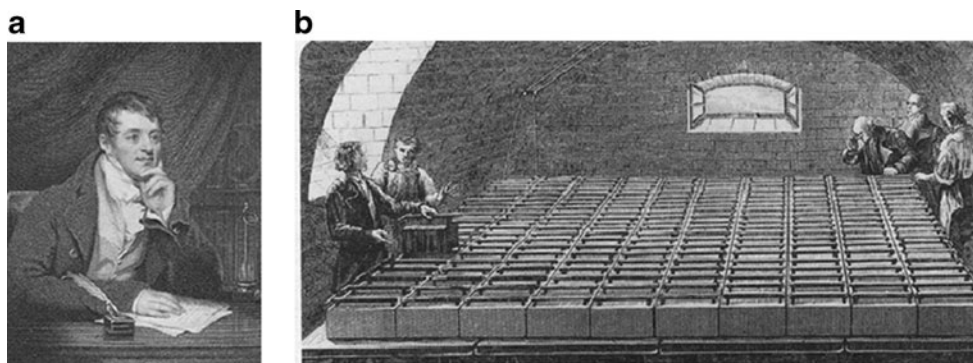
Fig. 9 **a** Alessandro Guisepe Antonio Anastasio Volta (1745–1827), **b** Volta (Voltaic) pile, **c** Volta's letter to The Royal Society



1797 and died in poverty on 4 December 1798. Nonetheless, his name is preserved in many expressions in electrochemistry such as: galvanic cell, galvanize, galvanometer, galvanostat, Galvani potential difference, galvanic corrosion and galvanoplastics. On the other hand, the historic term ‘galvanism’, which was used to signify the production of electricity by chemical reaction, is less used in electrochemical science nowadays.

In summary, the eighteenth century had witnessed a continuous stream of new ideas, discoveries and inventions. For instance: James Watt had introduced a more efficient version of Thomas Newcomen's steam engine that would transform the industrial world; by introducing the theory that chemical compounds are formed from elements, Antoine Lavoisier in his *Traité Élémentaire de Chimie* (published 1789) had swept away the last vestiges of the secret world of alchemy to herald the beginnings of modern chemistry; Captain James Cook and other navigators had brought back astonishing collections of plants and animals from great ocean voyages. It was the emergence of an ‘age of reason’, when writers and philosophers began to assert that informed rational thinking would banish mystical belief and superstition and usher in a new era of political and intellectual freedom, along with material progress. The transition became known as the ‘Enlightenment’ and the scientific phenomenon that overwhelmingly characterized this era was the production of electricity in useful quantities.

Fig. 10 **a** Sir Humphry Davy (1778–1829), **b** illustration of Royal Institution battery



Electrochemical science and battery technology gather pace

Electrolysis

Sir Humphry Davy (Fig. 10a), who was working at the Royal Institution in London, soon recognized that the Volta pile produces electricity via chemical reactions at the metal/solution interfaces: hydrogen is evolved on the ‘positive’ copper disc and zinc is consumed at the ‘negative’ disc. Indeed this recognition of the relationship between chemical and electrical effects prompted Davy to coin the word ‘electrochemical’, from which sprang the science of ‘electrochemistry’. He gave warning that Volta's work was ‘an alarm bell to experimenters all over Europe’. His prediction was soon to be verified.

Volta had sent his letter to the Royal Society in two parts because he anticipated problems with its delivery given that correspondence from Italy had to pass through France, which was then at war with Britain. While waiting for the second part to arrive, Joseph Banks had shown the first few pages to Anthony Carlisle (a fashionable London surgeon) who, in turn, with the assistance William Nicholson (a competent amateur scientist) assembled on 30 April 1800 the first pile to be constructed in England. Almost immediately, on 2 May 1800, the two investigators found that the current from their device was capable of decomposing water into its constituents of hydrogen and oxygen.

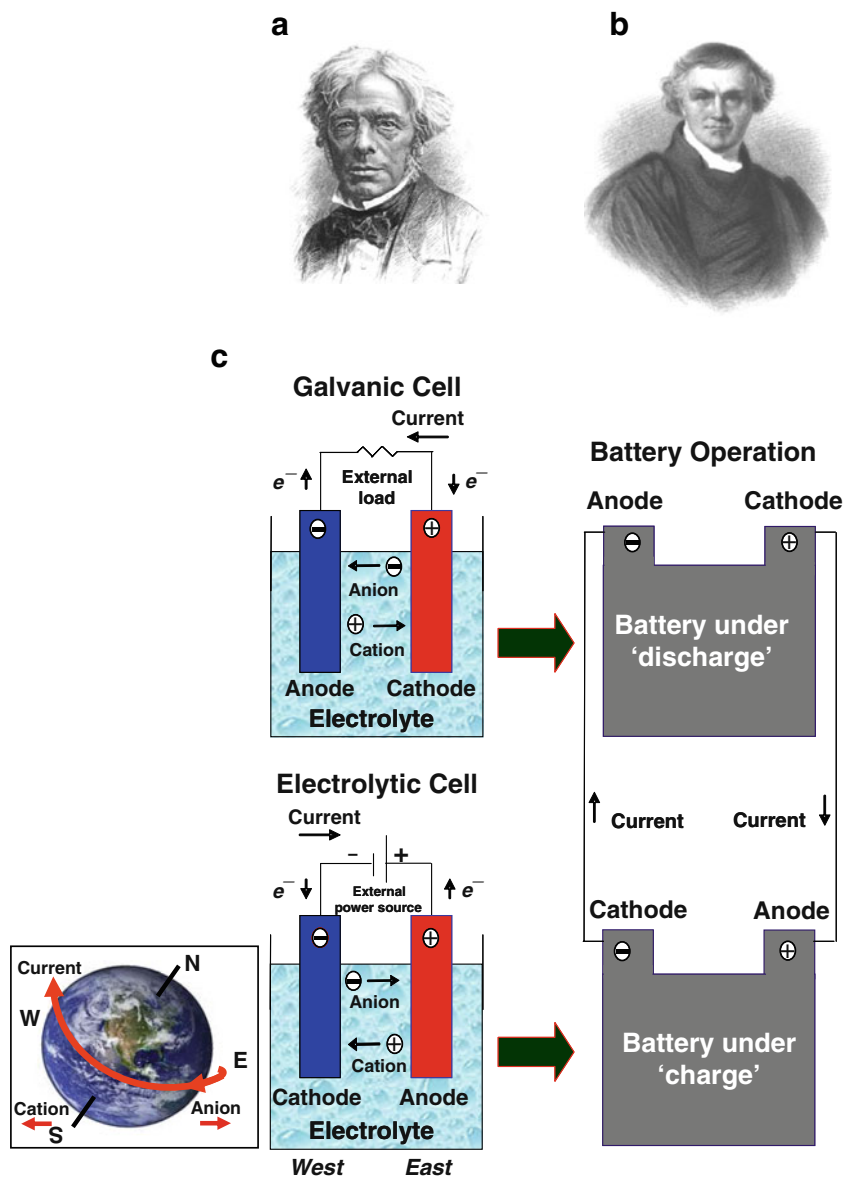
Details of the discovery were published in Nicholson’s own journal in the following July of the same year [11]. Thus, the new technique of ‘molecular splitting’—to be coined ‘electrolysis’ by Michael Faraday much later in 1834 and derived from the Greek ‘lysis’=separation—was demonstrated before Volta’s own account of the pile was made public in September 1800! It is not difficult to imagine the apoplectic effect that such a chain of events would have on present-day guardians of intellectual property! Meanwhile, Davy began to wonder whether electrolysis could also separate other substances into their elements [12]. To assuage his curiosity, an enormous battery of 2,000 pairs of discs was built in the basement of the Royal Institution (Fig. 10b), and with it Davy discovered potassium (1807), sodium (1807), barium (1808), boron (1808), calcium (1808) and magnesium (1808). He was also the first to

isolate strontium (1808) and to show that chlorine was an element.

Electrochemical nomenclature

It was left to Davy’s brilliant student—Michael Faraday—to identify the mechanisms of the processes that take place within ‘electrolytic’ cells and to give them a quantitative basis (Fig. 11a). In addition, he was also the guiding force behind the nomenclature that is still in use today. First, Faraday, with the assistance of Whitlock Nicholl, his personal physician and an accomplished linguist, devised the name ‘electrode’ to describe a solid substance at which an electrochemical reaction occurs. Then, to distinguish between the electrode by which conventional current enters an electrolytic cell and the electrode by which it leaves,

Fig. 11 **a** Michael Faraday (1791–1867), **b** William Whewell (1794–1866), **c** nomenclature used in the operation of electrochemical cells



Faraday sought the assistance of the polymath William Whewell, The Master of Trinity College at the University of Cambridge (Fig. 11b). In a letter dated 24 April 1834 [13], he asked Whewell:

‘Can you help me out to two good names not depending upon the idea of a current in one direction only or upon positive or negative?’

In other words, he wanted terms that would be unaffected by any later change in the convention adopted for the direction of current. Eventually, they settled on calling the positive electrode an ‘anode’ and the negative electrode a ‘cathode’, which were coined from Greek ‘ano-dos’ (‘upwards’—‘a way’) to represent the path of electrons from the positive electrode to the negative and ‘katho-dos’ (‘downwards’—‘a way’) to represent the counter-direction (Fig. 11c). For an electrolytic cell then, the anode is where the current enters the electrolyte on the East side and the cathode is where the current leaves the electrolyte on the West side. The use of ‘East’ and ‘West’ to mean the respective ‘in’ and ‘out’ directions of the current was somewhat contrived, namely:

anode → current in → electrons up → sunrise → East

cathode → current out → electrons in → sunset → West.

Further, Faraday set the orientation of the electrolysis cell so that the internal current would run in the same East→West direction as a hypothetical current flow that would be required to give the Earth its observed magnetic field. He detailed this decision in the following text that was also part of the abovementioned letter to Whewell.

‘If we admit the magnetism of the globe as due to electric currents running in lines of latitude, their course must be, according to our present modes of expression, from East to West and if a portion of water under decomposition by an electric current be placed so that the current through it shall be parallel to that considered as circulating round the earth, then the oxygen will be rendered towards the east and the hydrogen towards the west.’

Then, with the use of the Greek neutral present participle ‘ion’—‘a moving thing’—for migrating particles in electrolysis, two further terms were obtained, namely, ‘anion’, i.e. that which goes to the anode against the current (or with the flow of negative charge) and ‘cation’, i.e. that which goes to the cathode with the current (or against the flow of negative charge). The term ‘ion’ originates from the mythological Greek hero Ion, the son of Xuthus, who migrated from northwestern Thessaly to the Peloponnese and thence to Attica. The anode–cathode terminology for an ‘electrolytic

cell’ applies to a ‘battery under charge’ (secondary system, v. i.), whereas the reverse applies to a ‘galvanic cell’, or a ‘battery under discharge’ (primary or secondary system), that is, the anode now becomes the cathode and the cathode becomes the anode. Nevertheless, the directions of the migration of anions and cations with respect to current flow are unchanged, the positive electrode remains a positive electrode and the negative electrode remains a negative electrode.

Lead–acid battery scientists, technologists and manufacturers recognize that the two electrodes retain their respective polarities irrespective of whether a cell is charging or discharging and thus they universally and consistently favour the terms ‘positive electrode (or plate)’ and ‘negative electrode (or plate)’. Unfortunately, however, followers of other battery chemistries invariably refer to anodes and cathodes, but often erroneously. Similar mistakes are also to be found in scientific papers, textbooks and encyclopaedias. To prevent confusion, it is better to use the terms ‘cathodic’ and ‘anodic’ to describe currents and ‘positive’ and ‘negative’ to characterize electrodes. Not only does the latter terminology remain the same on discharge and charge but it is also particularly appropriate because the terminals of commercial cells and batteries (both primary and secondary) are clearly marked ‘+’ and ‘–’. It is regrettable that most textbooks fail to provide students of electrochemical science with a simple nomenclature aide-mémoire of the form given in Fig. 11c.

The Volta pile galvanized an enormous wave of research into different types of cell. It was soon realized that piles were awkward to use and that it was more convenient to immerse plates (or rods) of two different metals in a vessel that contained a suitable electrolyte solution. The first designs, such as those shown in Fig. 12a–c, employed single electrolyte solutions and they all exhibited a marked fall in voltage on the delivery of current. The reduced power output was attributed to an insulating effect that arose from the formation and collection of hydrogen bubbles on the positive (copper) electrode. Thereupon, extreme efforts were made to remove the hydrogen. The resulting techniques were mainly mechanical and included shaking, brushing, rotating or alternate raising/lowering (‘plunging’) of the plates. Some methods were dependent on manual operation, some on clockwork and (according to the optimistic claims of their inventors) some on using a part of the cell’s own energy output. The last-mentioned approach was adopted in the Humphreys design—a monster of a battery that consisted of 63 plates, which each measured 2 m by 1 m and were dipped into and pulled out of 945 gal of fuming nitric and sulfuric acids by a driven system of ropes and pulleys (Fig. 12d). Of course, a practical solution to the problem was to find an electrode reaction that proceeded at a potential at which the discharge of hydrogen was prohibited. In due course, this realization led to the development of ‘two-fluid’ systems that included

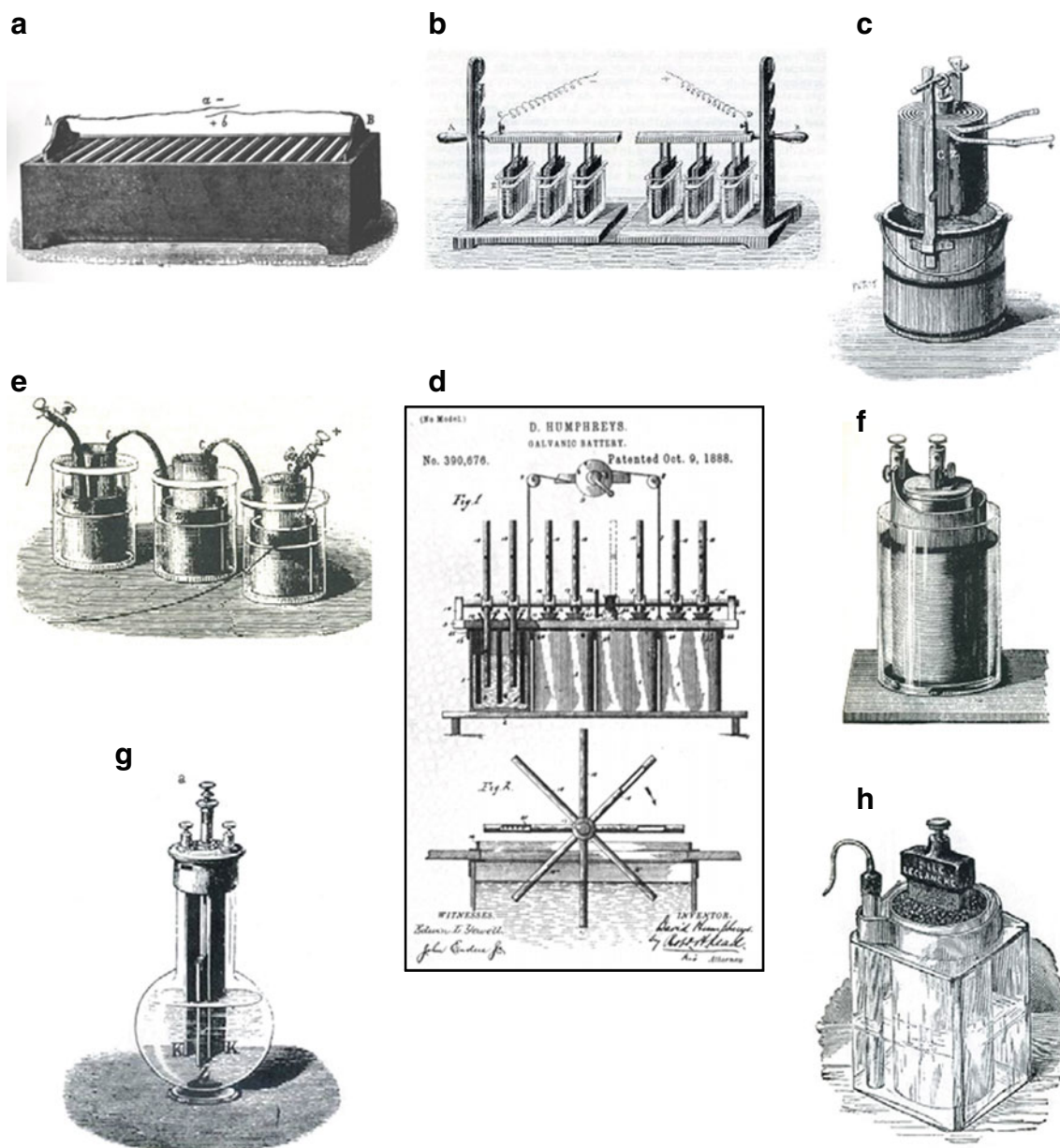


Fig. 12 Development of primary cells: **a** Cruickshank, 1800; **b** Wollaston, 1815; **c** Hare, 1819; **d** Humphreys, 1888; **e** Daniell, 1836; **f** Grove, 1838; **g** Poggendorff, 1842; **h** Leclanché, 1866

the famous Daniell and Leclanché cells (Fig. 12e–h). Because several of these cells ‘worked well’, i.e. there was little deviation from the thermodynamic values of the electrode potentials, those that did not ‘were regarded as dissident—thermodynamically reversible basically but befouled by some regrettable artefact of doubtful origin’, as neatly summarized by Bockris [14].

The curse of polarization

The departures from reversible thermodynamic voltages (i.e. ‘ideal’ behaviour) shown by cells upon the passage of current were attributed by classical electrochemists to an ill-defined

and misleading concept called ‘polarization’. It is not clear who first introduced this term. Michael Faraday, however, believed that electrolysis involved particles of the electrolyte first becoming ‘aligned or polarized’ in an electric field [15]—each particle was considered to undergo a separation of electric charge in a manner similar to the formation of north and south poles in a magnet. The electric field was then assumed to divide the contiguous particles into positive and negative ions which interoscillated, changed partners and reorientated to allow the flow of current through the electrolyte. In this way, the polarization was continuously counteracted and positive ions of the electrolyte were transported between the electrodes in one direction, and

negative ions in the other. Faraday then asserted that the particles of a non-conductor in an electric field would remain fixed in the polarized state and thus would not permit the transfer of charge. It should also be noted that, by analogy with magnetism, the solid substance that carries the current out of, or into, the electrolyte solution was commonly referred to as a ‘pole’. Although Faraday well appreciated the similarities between magnetic and electrical phenomena, it has proved fortunate that he considered pole to be a misleading name in the case of electrochemical cells and therefore, as outlined above, introduced the term ‘electrode’. Notwithstanding Faraday’s objection, pole still continues to be used to describe some forms of electrode, e.g. ‘bipolar’ designs that are employed in electrolysis cells, batteries and fuel cells.

It was later realized that the dissociation of electrolytes into positive and negative ions does not require the imposition of an electric field but occurs spontaneously on the dissolution of electrolytes in solvents. Polarization then became associated with any process which restricts current flow, and not with the formation of polarized particles.

The continued use of terminologies long after the ideas on which they are based have been proven inappropriate is also illustrated by the long-standing practice of adopting ‘carbon–zinc’ as the name for the common primary (Leclanché) battery. Early research showed that a cell comprised of a carbon and a zinc electrode in an aqueous electrolyte gave a poor electrical output. As discussed above for early primary cells, the formation of hydrogen bubbles at the positive electrode restricted the current flow and thereby was said to give rise to polarization. To avoid this problem, manganese dioxide was added to the carbon electrode. This material was deemed to function as a ‘depolarizer’ by oxidizing (i.e. removing) the hydrogen evolved on the carbon. It is now recognized that manganese dioxide itself is the electroactive material of the positive electrode and that the carbon simply acts as a current collector. As stated by Heise and Cahoon [16] in their classic text, *The Primary Battery*:

‘It is most unfortunate that oxidizing reagents should have been considered loosely, even in recent times, as ‘depolarizers’ acting by the oxidation of liberated hydrogen. They are actually the reactants determining the electrode potential and operating at voltages precluding the discharge of hydrogen.’

In 1889, Walther Nernst (Fig. 13a) disclosed a thermodynamic theory for the potential difference that is established across the electrode|electrolyte interface, i.e. the ‘equilibrium’ electrode potential [17]. His eponymous equation gave the first quantitative relationship between

this potential and the nature and state of both the electrode itself and the electrolyte. Electrode reactions became better understood during the 1920s and 1930s with the derivation of the Butler–Volmer equation [18, 19] which expresses the potential dependence of the rates of the forward and backward components of a given electrode reaction (Fig. 13b); it places the Nernst equation on a kinetic–mechanistic foundation by taking the rates of these opposing component reactions to be equal at equilibrium, i.e. when there is no net current flow. The Butler–Volmer equation also provides a theoretical explanation of the empirical expression for the kinetic behaviour of electrodes that had been introduced many years earlier by Julius Tafel [20] (Fig. 13c). For a detailed account of the development of electrode kinetics (see [21]).

In their seminal paper (mentioned above), Agar and Bowden [2] recommended the use of the term ‘overpotential’ [22] in order to:

‘avoid the general confusion which arises from the loose use of the word polarization.’

It should be noted that, in 1874, William Grove (the pioneer of the fuel cell, v.i.) had expressed a similar concern about the term polarization when reflecting on his earlier demonstration of the inactivity of amalgamated zinc electrodes in acid media. He stated [23]:

‘I know of no other word [polarization] to express the effect [...] the word is used in this sense by most French writers, but, from its numerous applications, is sadly inaccurate.’

Agar and Bowden distinguished three causes of the restriction in the current flow that is associated with electrode reactions. These are:

- ‘Activation overpotential’, which results from limitations imposed by the kinetics of charge transfer at the electrode.
- ‘Concentration overpotential’, which results from the kinetics of mass transfer of active materials to the electrode surface during the passage of current.
- ‘Resistance overpotential’, which results from the ionic resistance of the electrolyte and the electronic resistance of the other cell components.

The terms ‘potential’ and ‘overpotential’ should be used only for single electrodes with the corresponding terms ‘voltage’ and ‘overvoltage’ reserved for cells and batteries. In summary, overpotential refers to an individual electrode reaction and is the difference in the values of the actual electrode potential and the equilibrium (reversible) potential of the reaction under consideration.

Fig. 13 **a** Walther Hermann Nernst (1864–1941), **b** Max Volmer (1885–1965), **c** John Alfred Valentine Butler (1899–1977), **d** Julius Tafel (1827–1893)



Despite the advice of Grove and also of Agar and Bowden, as well as the developments in electrokinetic theory, the old concepts of polarization persisted. In 1971, for example, Bockris [14] declared overpotential to be ‘a lacuna in scientific knowledge’. He argued that the delay in the spread of knowledge of modern aspects of electrochemistry was unfortunate given the relevance of overpotential ‘to applied chemistry in the context of the necessity to avoid the continued injection of carbon dioxide and pollutants into the atmosphere.’ In concluding his article, Bockris advocated that:

‘The principal energy sources of the future will be solar, atomic, and geophysical, and hence energy will be available exclusively in the form of electricity. It will

also be very much cheaper than at present. It would be disastrous not to be prepared to use it. But its intelligent use—and our survival—at least in chemical processes, energy conversion, metallurgy, engineering, etc., depends on a widespread comprehension of the electrochemical concept of overpotential.’

These have proven to be prophetic words, given today’s mounting concern over global climate change and its relationship to increases in carbon dioxide emissions from the use of fossil fuels as prime energy sources.

Dictionaries continued, however, to define polarization in an unacceptable way. Inappropriate descriptions of polarization also appeared in many other reference sources and scientific publications. Regrettably, these

former ideas of polarization have continued to this day. Accordingly, every effort should be made to expunge this archaic expression, which does not consider the kinetic behaviour of the specific reactions occurring at electrodes, from the electrochemistry lexicon.

Realization of the first practical secondary cell (battery)

In 1802–1803, the German physicist Johann Wilhelm Ritter (Fig. 14a) found that a pile of copper discs layered with cardboard soaked in brine was able to generate a transitory ‘secondary’ current, after it had been charged electrically. Unfortunately, this observation was largely disregarded, mainly because Ritter’s latter studies of occult phenomena damaged his reputation as a serious scientist and, sadly, he died at the early age of 33.

Given the great enthusiasm for cell and battery science after 1800, it is rather surprising that over 50 years were to pass before meaningful attempts were made to produce a secondary, i.e. rechargeable, battery. The systems under study were all based on lead. In 1851, Charles William Siemens (Fig. 14b; born Carl Wilhelm Siemens, in Germany) made the first prototype lead–acid battery by plating the metal from a lead acetate solution on to cylindrical carbon electrodes [24]. The cylinders were dried, heated to redness and then cooled, with repetition of the process until a substantial build-up of lead monoxide was obtained. Two cylinders were then immersed in a dilute solution of sulfuric acid and current was passed through them until the lead monoxide on one cylinder was converted to lead dioxide and that on the other to metallic ‘spongy’ lead. Siemens soon abandoned this work, however, because he found the process of charging the cell from Grove

Fig. 14 **a** Johann Wilhelm Ritter (1776–1810), **b** Charles William Siemens (1823–1883), **c** Wilhelm Josef Sinsteden (1823–1883)



batteries (Fig. 12f) to be: ‘too expensive to render the secondary battery available for practical purposes’. In fact, he did not publish his results until 1881 [25].

Meanwhile, Wilhelm Josef Sinsteden (Fig. 14c) had been developing and building an electromagnetic generator to enable the operation of long telegraph lines. To measure the current strength of his device, he passed the output between pairs of lead, nickel or silver plates immersed in dilute sulfuric acid or zinc-saturated potassium hydroxide solutions. Although he favoured the silver-in-acid system, he also noted that a cell made from two lead plates in acid solution was effective in storing current and gave a good discharge. Nevertheless, after publishing his results in 1854, he too discontinued investigations of electrochemical cells.

Five years later, Gaston Planté (Fig. 15a), whilst working for the Paris electrometallurgical firm of Christofle, commenced a systematic search of metals that he thought would prove effective for the useful conversion and storage of energy via electrochemical means. Following an exhaustive search of the literature, Planté restricted his investigations exclusively to systems based on the use of sulfuric acid electrolyte solutions. He evaluated the performance of different metals by suspending a pair of identical wires of each candidate in a beaker that contained 10 wt.% sulfuric acid solution. The assembly was charged by Grove nitric acid cells and then discharged through galvanometers that had varying degrees of sensitivity. The charge and discharge currents for each metal were recorded, along with the physical appearance and

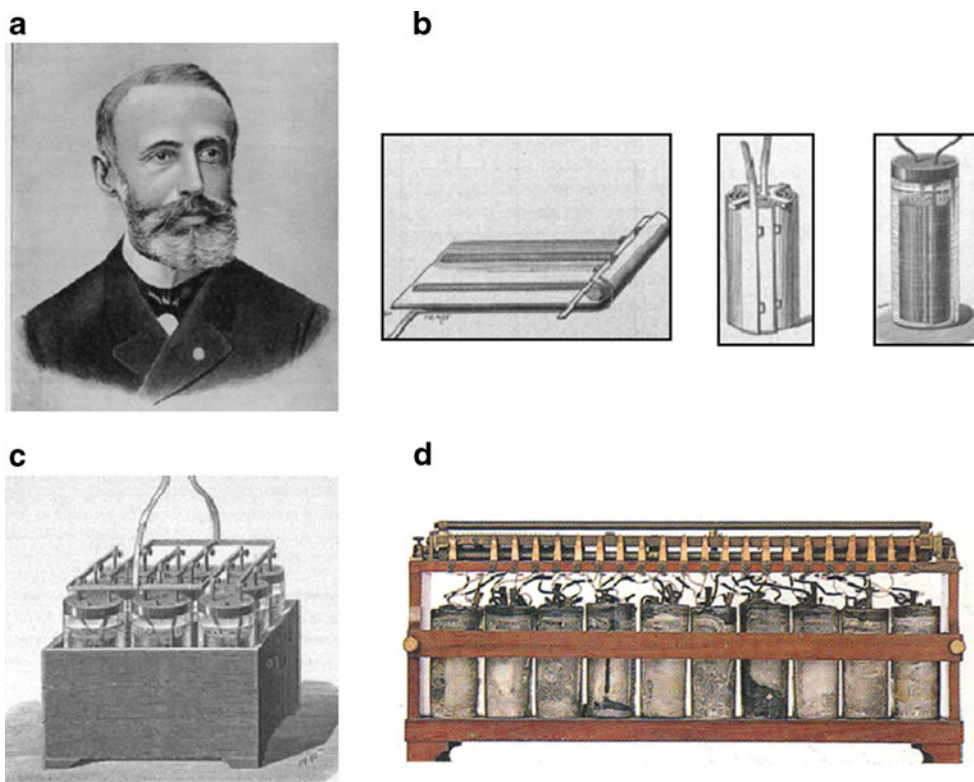
behaviour of the wires. In terms of decreasing secondary currents and of decreasing power to resist the charging current, Planté ranked the metals as follows:

Secondary currents (strongest at top)	Resistance to charging current (strongest at top)
Silver	Aluminium
Lead	Tin
Tin	Lead
Copper	Copper
Gold	Silver
Platinum	Gold
Aluminium	Platinum

Though silver exhibited the most powerful secondary current, it was unsuitable for a battery as it dissolved from the positive electrode during charging; a similar behaviour was exhibited by tin and copper. Gold and platinum were rejected as being too expensive, and aluminium gave the weakest secondary current. Lead was the only metal remaining and Planté found it to be acceptable—both the metal itself and its oxides were virtually insoluble in dilute sulfuric acid solution, and lead dioxide was a good conductor and adhered strongly to the lead substrate from which it was formed.

Taking inspiration from the popular design of earlier primary cells, Planté loosely rolled together two thin sheets of lead separated by a sheet of flannel or rubber strips and then

Fig. 15 **a** Raymond Louis Gaston Planté (1834–1889); **b** Gaston Plante’s illustrations of his seminal design of lead–acid cell and **c** a battery of nine such cells [27]; **d** an early battery of Planté cells



inserted the cylindrical assembly into a glass jar of the same geometry that contained a dilute (10 wt.%) solution of sulfuric acid (Fig. 15b). The plates were charged for about 24 h by a primary battery. A brown coating of lead dioxide (PbO_2) was formed on the positive and oxygen was evolved, whereas the appearance of the negative remained unchanged but hydrogen was liberated. Planté found the device to be: ‘a secondary element of great power’. Repeated charge and discharge operations were found to improve the cell performance. On 26 March 1860, Planté demonstrated a battery of nine such cells to members of the French Academy of Sciences [26] (Fig. 15c). He wrote later that: ‘by passing through this apparatus the current from five small Bunsen cells, we obtained a very bright spark when the two terminal wires of the battery were brought into contact for an instant’ [27]. The invention proved to be the world’s first practical secondary battery.

Whereas it should be recognized that Gaston Planté did not originate the concept of the lead–acid battery—he was anticipated by Siemens and Sinsteden, as discussed above—he was the first to carry the system to a full elaboration. Gaston Planté therefore deserves to be regarded as the ‘Father of the storage battery’ for he showed how to convert the physical and electrochemical phenomena observed by Siemens and Sinsteden into techniques that enabled the manufacture of a useful device for the storage of electrical energy.

The basic discharge–charge reactions of the lead–acid cell involve dissolution–precipitation mechanisms (Fig. 16a). During discharge, sulfuric acid is consumed and lead sulfate (PbSO_4) is formed at both plate polarities; the processes are reversed on charging. As the cell approaches full charge, the majority of the PbSO_4 will have been converted back to Pb or PbO_2 and a further passage of current gives rise to the evolution of hydrogen at the negative electrode and oxygen at the positive electrode, as shown in Fig. 16b. The gases are released in stoichiometric proportions and, with traditional cell designs, result in a loss of water from the cell.

It should be noted that the lead–acid cell is able to operate effectively as an energy storage device by virtue of three critical factors. First, contrary to thermodynamic expectations, the liberation of hydrogen from acids by lead takes place at only a negligible rate, i.e. there is a high hydrogen overpotential (see Fig. 16b). Second, the high oxygen overpotential at the positive electrode allows lead sulfate to be converted to lead dioxide before appreciable evolution of oxygen commences (see Fig. 16b). Third, although the solubility of lead sulfate in the electrolyte is sufficient to promote the electrode dissolution–precipitation reactions, the value is so low that there is little migration of the material during charge–discharge cycling and, hence, a high degree of reversibility is maintained.

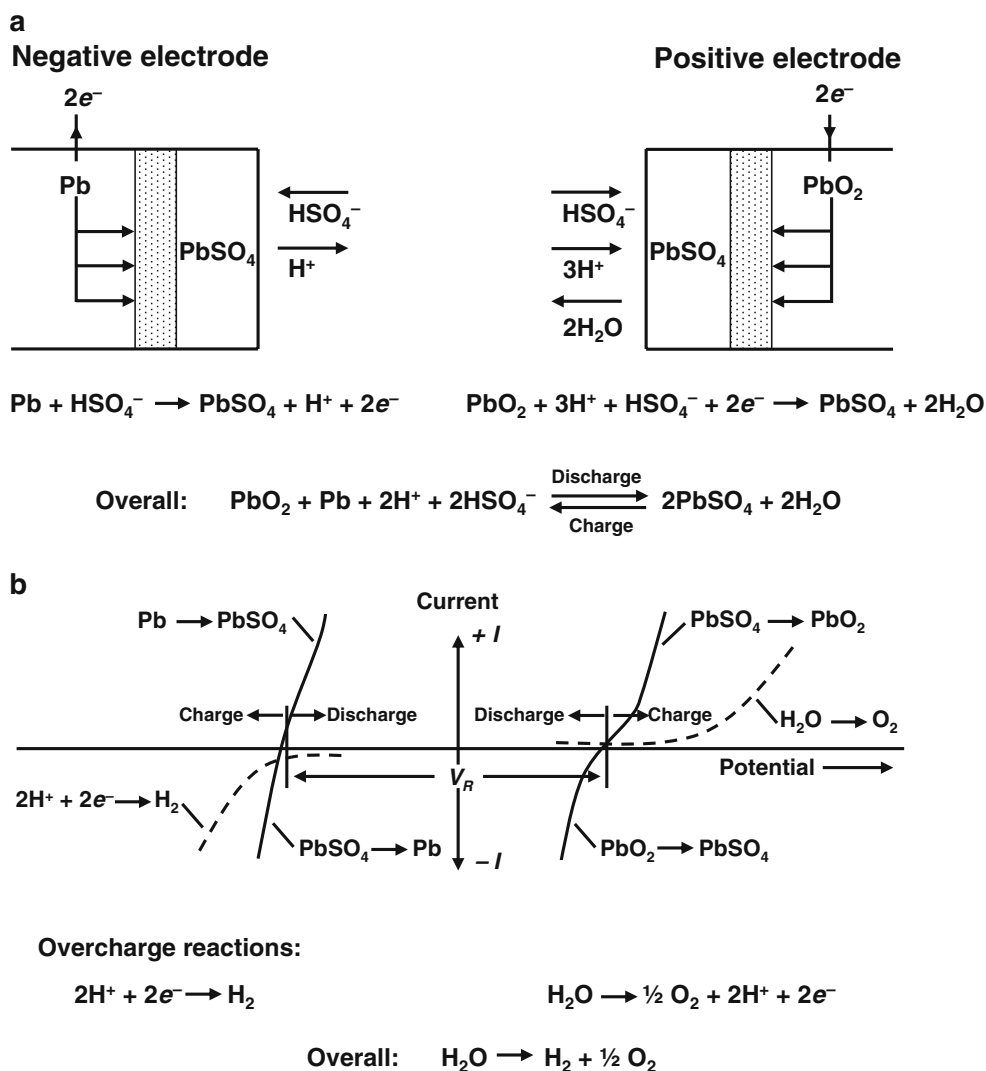
The full capability of the lead–acid battery as an electrochemical power source was not realized immediately because only primary cells were available for charging, and these gave relatively weak currents and soon became exhausted (Fig. 17a). It was not until 1871 that Zénobe Gramme revealed, also to the French Academy of Sciences, the first generator to provide power on an industrial scale (Fig. 17b, c). The machine was mass produced by Breguet, a maker of scientific, electrical and telegraphic apparatus. In due course, the same company became the first to manufacture Planté batteries (Fig. 15d).

The basic components required for the establishment of an electrical power industry—the electric motor, the transformer and the dynamo—had been discovered some 50 years earlier by Michael Faraday (Fig. 18a). Faraday had in fact created both halves of the industry: he had found that electric current can generate movement (the motor) and that movement can generate electricity (the dynamo). It was not, however, until the invention of the incandescent light bulb by Joseph Wilson Swan in England (1878; Fig. 18b) followed by its improvement by Thomas Edison in the USA (1879; Fig. 18c) and the appearance of the Parsons compound steam turbine (1884) that the burgeoning demand for plug-in electricity prompted the construction of large coal-fired power stations and distribution systems. Understandably, the availability of industrial-scale electricity was accompanied by a rapid expansion in the production of lead–acid batteries. Two alkaline storage batteries also appeared, namely, the nickel–cadmium and nickel–iron systems that were invented, respectively, by Ernst Waldemar Jungner from Sweden in 1899 and Thomas Edison in 1901. Both designs employed an electrolyte of potassium hydroxide and a positive electrode of nickel oxide. Due to high material costs, however, these two batteries failed to enjoy the same degree of market success as lead–acid.

The evolution of the lead–acid battery

A decisive step in the commercialization of the lead–acid battery was made by Camille Alphonse Faure who, in 1880, coated the lead sheets with a paste of lead oxides, sulfuric acid and water. On ‘curing’ the plates at a warm temperature in a humid atmosphere, the paste changed to a mixture of basic lead sulfates that formed an adequate bond with the lead electrode. During charging, the cured paste was converted into electrochemically active material (or the ‘active mass’) and, compared with the Planté procedure, offered a faster ‘formation’ process and a substantial increase in cell capacity. Soon the idea of punching rectangular holes out of the lead plates to yield grids of lighter weight and to provide receptacles into which the paste could be packed was developed. So was born the modern ‘pasted-plate battery’, which is by far the

Fig. 16 Schematic representation of **a** electrochemical processes during discharge of a lead–acid cell and **b** current–potential characteristic of each electrode



most common type of lead–acid battery in use today (note, various other methods are now used to fabricate the grids). An alternative cell design employs positive plates in which the active material is contained in tubes, each fitted with a coaxial current-collector; the concept was conceived by SC Currie in 1881. Such ‘tubular plates’

constrain the active material and reduce its tendency to expand, disconnect and shed during battery duty. Despite the fact that this plate configuration adds to the complexity, and therefore to the cost, of the manufacturing process, tubular batteries have found some use in heavy charge–discharge operations.

Fig. 17 Charging Planté cells with **a** Bunsen cells and **c** a Gramme magneto generator, **b** Zénobe Théophile Gramme (1826–1901)

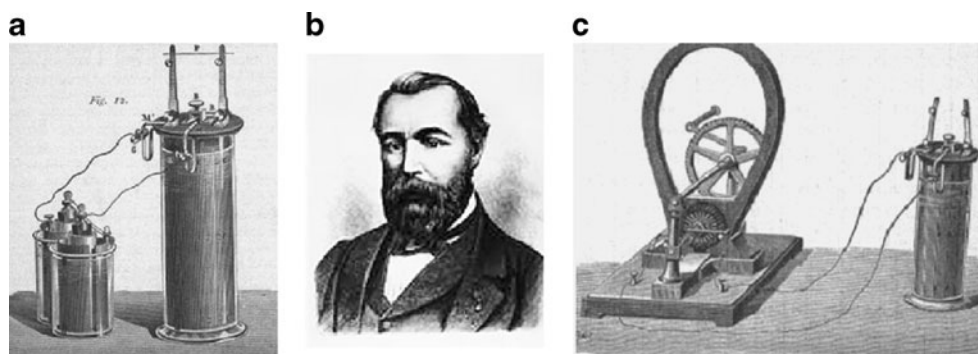
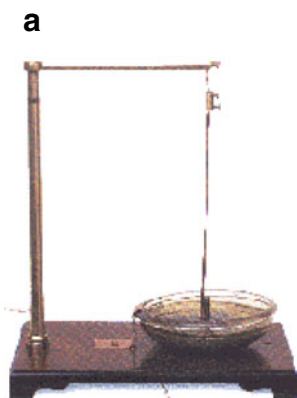


Fig. 18 **a** Faraday's electromagnetic discoveries that were to change the course of history, **b** Joseph Wilson Swan (1828–1914), **c** Thomas Alva Edison (1847–1931) holding his incandescent light bulb (within superimposed *white circle*)



The first electric motor
22 December 1821



The first transformer
29 August 1831



The first dynamo
August – November 1831



The initial demand for lead–acid batteries was to provide emergency power to essential equipment in electricity-generating stations and at other critical sites. For such large ‘standby-power’ applications, it is notable that no other battery chemistry has been able to compete on cost grounds with the lead–acid system. Towards the end of the nineteenth century, electric cars appeared on the roads and were powered mostly by lead–acid. The batteries also began to be used for illumination in railway coaches, as well as to power railway signalling systems, the electrical equipment of ships and radio receiving–transmitting equipment. With the advent of the internal combustion engine, the ‘automotive’ lead–acid battery was first employed in road vehicles for lighting, then also for engine starting, and now additionally for the whole range of electrical duties expected in the modern vehicle. Ironically, it was the invention of the electric self-starter by Charles F Kettering in 1911 that contributed to the demise of the electric battery car!

By 1910, the construction of lead–acid batteries involved the use of an asphalt-coated and sealed wooden container, wooden separators, thick plates and inter-cell connections made through the cover by means of heavy lead posts and links. The first important change came in the early 1920s when the more acid-resistant, hard rubber case was developed and introduced. During the next 40 years,

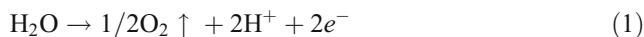
basic battery construction changed little, although active material performance was enhanced through the introduction of additives and superior raw materials. Significant advances were also made in grid technology. Back in 1881, J Scudamore Sellon had demonstrated the benefits to be gained by replacing the pure-lead grids of Faure-type plates with lead–antimony counterparts. In the industry, this became known as a change from ‘soft lead’ to ‘hard lead’, and as much as 11 wt.% antimony was present in the latter. Antimony serves to improve the castability, hardness, strength and creep resistance of the grid; thereby, it allows the handling of thinner grids. The element also exerts a subtle yet beneficial effect on both the structure and the life of the positive active material, particularly under severe conditions of charge–discharge cycling. There is, however, a major disadvantage with using antimony. During battery charge, antimony dissolves (corrodes) from the positive grid, diffuses through the electrolyte and deposits on the negative plate where it lowers the overpotential for hydrogen evolution and thus causes greater rates of gassing, water loss (therefore, more frequent ‘topping-up’ maintenance) and self-discharge, v.i. Increases in the efficiency of the manufacturing process were also achieved between 1910 and 1950, especially following the inception of technology for the machine pasting of plates.

In the late 1950s, one-piece covers that were epoxy-sealed to the cases were introduced. The case and cover material, however, remained hard rubber and inter-cell connections were still made through the cover. Lower-resistance separators, which were made of cellulose fibre impregnated with phenolic resin, also came into use and obviously raised the electrical performance of cells. Machine stacking of plates became common and reduced the level of manual labour involved in cell assembly. Alloys with less than 2 wt.% antimony were developed and contained a small amount of selenium (0.02 wt.%) as a grain refiner to add strength and to enhance the resistance to corrosive attack. This alloy markedly lowered the rate of water loss (as well as raw material costs) and eventually resulted in the appearance of ‘low-maintenance’ batteries for the automotive market.

In the early 1960s, a method was devised for automatically casting a busbar to join plates of the same polarity within a cell element. A technique for connecting the cells within a battery in series through the cell walls was also perfected. These improvements significantly decreased both the internal electrical resistance and the amount of connecting or ‘top’ lead required. Advances were also made in plate design and production techniques, which together gave rise to more efficient batteries with higher specific power. In the late 1960s, the injection-moulded polypropylene case and cover were instituted and provided the lead–acid battery with a durable, thin-walled, lightweight container. Moreover, the decrease in the thickness of the walls and cell partitions permitted the inclusion of a greater amount of active material without increasing the external weight or volume of the battery. Finally, the performance and the life of the batteries were both enhanced through the availability of low-resistance, highly durable plastic separators. Nevertheless, a technological explosion was waiting in the wings!

Classical lead–acid batteries are ‘flooded’ systems. That is, the electrolyte medium is a free liquid to a level above the top of the plates and above the busbars. This has the disadvantage that the cells have to be vented to release the oxygen and the hydrogen liberated during charging. As a consequence, not only is water lost (and has to be replaced on a regular basis) but also the battery can be used only in the upright position; otherwise, leakage of sulfuric acid solution takes place. In addition, the released gases carry a very fine mist of sulfuric acid that is highly corrosive. Efforts were therefore made to develop ‘sealed’ batteries that would not require topping up with water and would be safe under all conditions of use and abuse. At first, attention was directed towards the catalytic recombination of the gases within the battery, but this idea proved to be impractical. Success was eventually achieved through the invention of the ‘valve-regulated’ lead–acid (VRLA) battery. In this

design, oxygen evolved during the latter stages of charging, and during overcharging, of the positive electrode, i.e.



transfers through a gas space to the negative electrode where it is reduced (‘recombined’) back to water:

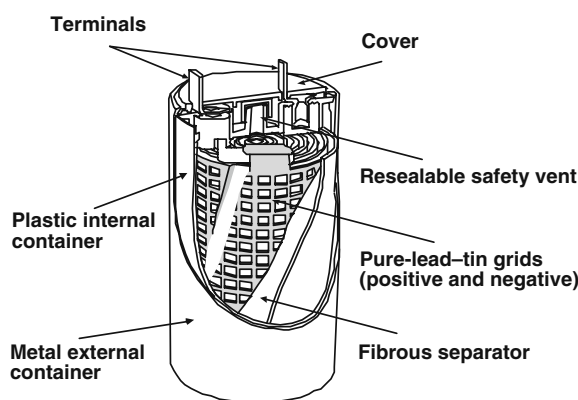


The process is known, variously, as the ‘internal oxygen cycle’, the ‘oxygen recombination cycle’, and the ‘internal oxygen–recombination cycle’.

There are two techniques for providing the gas space in a VRLA cell. One approach has the electrolyte solution immobilized as a gel (through the addition of fumed silica); the other has the electrolyte solution held within an absorptive glass mat (AGM), which also serves as the separator. Gas passes through fissures in the gel or through channels in the AGM. A corresponding recombination cycle for hydrogen is not possible since the oxidation of the gas at the positive electrode is far too slow. This feature, together with the fact that oxygen recombination is not complete (the efficiency is typically 93% to 99%), requires each cell to be fitted with a one-way valve as a safeguard against excessive pressure build-up—hence, the term ‘valve-regulated’. Antimony is not included in the grid alloys of VRLA cells because, as discussed above, this element lowers the hydrogen overpotential and exacerbates gassing at the negative electrode during charging. Care must be taken against the presence of other elements (typically, as trace impurities) that might act similarly. Today, lead–calcium–tin alloys are preferred by manufacturers of VRLA batteries for float duties and lead–tin for cycling applications. The ‘spill-proof’ VRLA battery can be employed in any orientation (upright, on its side or even upside down) and thus gives engineers a much greater degree of flexibility in the design of equipment.

The first commercial VRLA cells were introduced by Sonnenschein GmbH in the late 1960s [28] and by Gates Energy Products, Inc., in 1971 [29, 30]. These were, respectively, the gel and the AGM technologies. The initial Gates product, a D cell known as the Cyclon™, had a single pair of positive and negative plates which were interleaved with a microfibre–glass separator and wound together in a cylindrical can (Fig. 19); ironically, this arrangement mimicked that invented originally by Planté (Fig. 15b). Valve-regulated lead–acid batteries (AGM designs) are now employed in transportation for the starting of internal combustion engines and the powering of all the ancillary electrical equipment in vehicles. As stationary units, both AGM and gel batteries provide emergency power supplies in hospitals, hotels, factories, supermarkets, computer centres,

Fig. 19 a Schematic of the Cyclon™ valve-regulated lead–acid cell, together with a representative cell now produced by EnerSys



telephone exchanges and wherever it is vital to preserve a continuity of supply when the main electricity fails. Detailed information on VRLA battery science, technology and applications is to be found in [31].

In summary, with the advent of electricity utilities, Planté's invention became a universal means of storing electrical energy under a wide variety of duties. Indeed the entire civilized world as we know it today is totally reliant on this electrochemical technology. The modern lead–acid battery is a far cry from Planté's original experimental design, although the basic chemistry is unchanged. It is likely that this battery will play an important role in powering increasing numbers of hybrid electric cars (v.i.), as well as in storing renewable energy. These are important pathways to securing a sustainable future for mankind, as discussed below.

Other secondary cells (batteries)

In the years following the appearance in the marketplace of the lead–acid, nickel–cadmium and nickel–iron batteries, electrochemists searched the Periodic Table for new galvanic combinations of elements, or re-investigated previously documented systems, that would yield superior electrochemical performance with a long cycle life for a given application. Although stored energy and peak power per unit mass are the most commonly cited numerical values in the promotion of a so-called advanced system, it should be emphasized that these are not necessarily the most important criteria for a particular service. Even more significant considerations may be initial cost, overall electrical efficiency, reliability and freedom from maintenance, performance under fluctuating ambient temperatures, and effective lifespan under deep-discharge cycling.

In addition to the further development of the lead–acid battery (as discussed above), the following five classes of secondary battery have received the most attention as possible candidates for a wide variety of energy storage applications: alkaline (nickel–iron, nickel–cadmium, nick-

el–zinc, nickel–metal-hydride), flow (zinc–bromine, vanadium redox), mechanically rechargeable metal–air (zinc–air), high temperature (sodium–sulfur, sodium–nickel-chloride) and rechargeable lithium (lithium-ion, lithium–polymer). The key parameters of the various battery chemistries are summarized in Table 1. Detailed information on the history, operating principles and prospects of these systems are reviewed elsewhere in this issue of the *Journal of Solid State Electrochemistry* and in [32, 33]. Remarkably, nickel–metal-hydride and rechargeable lithium are the only new systems to have achieved commercial success.

Most of the inorganic electrochemical couples that are likely to be economically and commercially viable have now been investigated, with the possible exception of alternative intercalation electrodes and electrolytes for lithium batteries (e.g. lithium-ion, 'plastic' lithium, lithium–polymer, lithium–sulfur and lithium–air systems). It is doubtful that radically new electrochemical couples will emerge. Nevertheless, there is still an enormous scope for improving further the batteries already in existence by means of superior materials and better methods of construction and quality control. Even the lead–acid battery, after 150 years of history, is still being improved, as will be seen below.

Fuel cells

There is some debate over who discovered the principle of the fuel cell. In a letter written in December 1838 and published in the January–June 1839 issue of *The London and Edinburgh Philosophical Magazine and Journal of Science* [34], the German scientist Christian Friedrich Schönbein (Fig. 20b) described his investigations on fluids that were separated from each other by a membrane and connected to a galvanometer by means of platinum wires. In the tenth of 14 reported tests, one compartment contained dilute sulfuric acid in which hydrogen was dissolved, whereas the other compartment contained dilute sulfuric acid which was exposed to air. Schönbein

Table 1 Summary of secondary battery characteristics

Battery	Specific energy (W h kg ⁻¹)	Peak power (W kg ⁻¹)	Status
Lead–acid	35–50	150–400	Widely used; cheapest available
Nickel–iron	50–60	80–150	Low electrical efficiency; high self-discharge
Nickel–cadmium	40–60	80–150	Commercially available, but costly; recycling issues with toxic cadmium
Nickel–metal-hydride	60–80	200–300	Available in small-to-medium sizes; used in hybrid electric vehicles; costly
Nickel–zinc	70–100	170–260	Short cycle life
Zinc–bromine	70–85	90–110	Chemical reactivity of bromine to cell components; safety; development almost ceased
Zinc–air	100–200	80–100	Mechanically rechargeable only; development almost ceased
Vanadium redox	20–30	110	At demonstration stage for stationary energy storage
Sodium–sulfur	150–240	230	Development almost ceased
Sodium–nickel-chloride	90–120	130–160	Battery electric vehicle applications
Lithium-ion	100–220	200–1,000	Commercially available in small sizes; careful control of recharging required; various systems according to electrode and electrolyte materials employed

The values for specific energy and peak power are broad-brush only and depend almost as much on the design of the battery as on its chemistry. The theoretical limit to the specific energy of a battery is set by the free energy of the electrochemical reaction (which determines the cell voltage), the number of electrons transferred in the reaction and the mass of the electrodes. Generally, the theoretical cell energy, calculated in this way, is three to five times of that practically achievable. The reason for this huge discrepancy is that the practical value has to take account of the mass of all the other cell components (electrolyte, separators, container, current-collectors, terminal posts, etc.), as well as the coulombic inefficiencies arising from side reactions, such as corrosion and self-discharge, and voltaic inefficiencies associated with overpotential and resistive losses

detected current and concluded that this was caused ‘by the combination of hydrogen with (the) oxygen (contained dissolved in water)’. This discovery was largely overlooked, however, after the publication of a letter from William Robert Grove, a Welsh lawyer and a scientist at the Royal Institution (Fig. 20a). This was dated 14 December 1838, appeared a few pages later in the same journal [35] and described his evaluation of electrode and electrolyte materials for use in batteries. Apparently, it is unknown which article was written first, as Schönbein did not date his letter in full. In fact, this chronology is of little importance given the following postscript that Grove added to his letter in January 1839.

I should have pursued these experiments further, and with other metals, but was led aside by some experiments with different solutions separated by a diaphragm and connected by platinum plates; in many of these I have been anticipated.

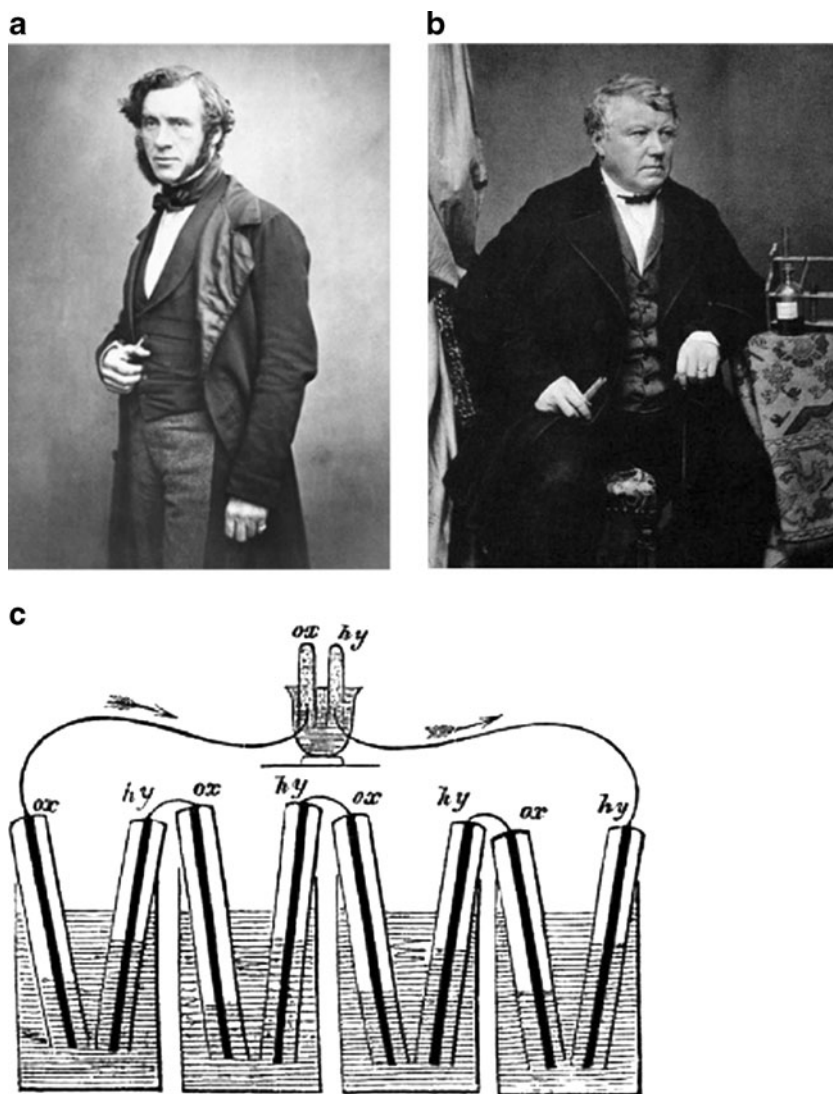
I will however mention one which goes a step further than any hitherto recorded; and affords, I think, an important illustration of the combination of gases by platinum.

Two strips of platinum 2 inches long and three-eighths of an inch wide, standing erect at a short distance from each other, passed, hermetically sealed, through the bottom of a bell glass; the projecting ends were made to communicate with a delicate galvanometer; the glass was filled with water acidulated

with sulphuric acid, and both the platina strips made the positive electrodes of a voltaic battery until perfectly clean, &c.; contact with the battery having been broken, over each piece of platinum was inverted a tube of gas, four-tenths of an inch in diameter, one of oxygen, the other of hydrogen, acidulated water reaching a certain mark on the glass, so that about half of the platina was exposed to the gas, and half to the water. The instant the tubes were lowered so as to expose part of the surfaces of platinum to the gases, the galvanometer needle was deflected so strongly as to turn more than half round: it remained stationary at 15°, the platinum in the hydrogen being similar to the zinc element of the pile. When the tubes were raised so as to cover the plates with water, the needle returned slowly to zero, but at the instant that the tubes were lowered again, it was again deflected; if the tubes were changed with regard to the platina, the deflection was to the contrary side.

The action lowered considerably after the first few minutes, but was in some degree restored every time the tubes were raised so as to wash the surface of the platina, and again lowered. After 24 hours, the water had risen half an inch in the tube containing hydrogen, and three eighths of an inch in that containing oxygen. In two other tubes, without platina, but with the same gases and immersed in acidulated water for the same time, the water had scarcely perceptibly risen, the effect therefore could

Fig. 20 **a** William Robert Grove (1811–1896), **b** Christian Friedrich Schönbein (1799–1868), **c** Grove's sketch of 4 cells of his gaseous voltaic battery (1842) [36]



not have been due to solution; the same sheets of platinum were exposed to atmospheres of common air and of similar gases, i.e., both to oxygen or both to hydrogen, &c., but without affecting the galvanometer. The platinum in the hydrogen was made the positive, and that in the oxygen the negative electrode of a *single* voltaic pair; the water now rose at the rate of three-eighths of an inch per hour in the hydrogen tube and proportionally in the oxygen; when the platina was not assisted by a pair of metals the oxygen was absorbed in more than its relative proportion. I hope, by repeating this experiment in series, to effect decomposition of water by means of its composition.'

In summary, when the tubes were lowered over the electrodes, the gases displaced the electrolyte solution to leave a thin layer of the acid solution on each electrode and the galvanometer indicated a flow of electrons between the two electrodes. The current decreased after a short period

but was restored by renewing the layer of electrolyte solution. Later, in 1842, Grove realized [36] that the reaction was dependent on an area of contact between the gas reactant and a layer of liquid which was thin enough to allow the gas to diffuse to the solid electrode (today, this requirement is commonly related to the formation of a 'three-phase boundary' or 'triple-point junction' where gas, electrolyte and electrocatalyst come into simultaneous contact). At that time, Grove was the Professor of Experimental Chemistry at the London Institution in Finsbury Circus and in the same communication [36] he reported the invention of a 'gaseous voltaic battery'. The device employed two platinized platinum electrodes (to increase the real surface area) and a series of 50 such pairs when semi-immersed in dilute sulfuric acid solution was found 'to whirl round' the needle of a galvanometer, to give a painful shock to five persons joining hands, to give a brilliant spark between charcoal points and to decompose hydrochloric acid, potassium iodide and acidulated water; an original

sketch of four such cells is reproduced in Fig. 20c. It was also found that 26 cells were the minimum number required to electrolyze water. Grove had indeed realized the desire expressed in his 1839 postscript in that he had achieved the beautiful symmetry inherent in the ‘decomposition of water by means of its composition’.

The above apparatus became widely recognized as the first fuel cell and Grove was designated as the ‘Father of the fuel cell’. Historically, this title is not fully justified. More accurately, Schönbein should be credited with the discovery of the fuel cell effect in 1838 and Grove with the invention of the first working prototype in 1842. Happily, such accreditations were of little concern to the two scientists and they became close friends. For almost 30 years, they exchanged ideas and developments via a dynamic correspondence and visited each other frequently.

It is interesting to note that many latter-day authors have attributed the introduction of the term ‘fuel cell’ to Ludwig Mond and Charles Langer in their description of a new form of gas battery in 1889 [37]. Remarkably, however, there is no mention of ‘fuel cell’ in this communication. Other claims that William W. Jacques, in reporting his experiments to produce electricity from coal [38], coined the name are equally ill-founded. AJ Allmand in his book *The Principles of Applied Electrochemistry* [4], published in 1912 (see Fig. 2), appears to attribute the appellation ‘fuel cell’ to the Nobel Laureate Friedrich Wilhelm Ostwald in 1894 (Fig. 21).

Grove concluded his short paper in 1842 [36] with the following modest entreaty:

‘Many other notions crowd upon my mind, but I have occupied sufficient space and must leave them for the present, hoping that other experimenters will think the subject worth pursuing.’

Unfortunately, however, the invention of the first internal combustion engine to become commercially successful by Jean Joseph Étienne Lenoir in 1859 coupled ironically with a discovery made by an electrochemist,



Fig. 21 Friedrich Wilhelm Ostwald (1853–1932)

namely, Michael Faraday, diverted the course of electricity generation from electrochemical to electromagnetic methods. As a result, the fuel cell became merely an object of scientific curiosity. In 1894, a well-documented criticism against heat engines was expressed by Ostwald who drew attention to the poor efficiency and polluting problems associated with producing electrical power via the combustion of fossil fuels rather than by direct electrochemical oxidation [39]. A fuel cell is inherently a more thermodynamically efficient device since, unlike an engine in which heat is converted to mechanical work, the cell does not obey the rules of the Carnot cycle. By virtue of this cycle, the efficiency of a thermal engine is always lowered to a value far below 100%, as determined by the difference between the temperature at which heat is taken in by the working fluid and the temperature at which it is rejected. On this basis, Ostwald advocated that:

‘The path which will help to solve this biggest technical problem of all, this path must be found by the electrochemistry. If we have a galvanic element which directly delivers electrical power from coal and oxygen, [...] we are facing a technical revolution that must push back the one of the invention of the steam engine. Imagine how [...] the appearance of our industrial places will change! No more smoke, no more soot, no more steam engine, even no more fire, [...] since fire will now only be needed for the few processes that cannot be accomplished electrically, and those will daily diminish. [...] Until this task shall be tackled, some time will pass by.’

Regrettably, Ostwald was proven to be correct as regards his closing prediction for although further attempts were made in the early 1900s to develop fuel cells that could convert coal or carbon into electricity [40–44], the need for an expensive platinum catalyst and its poisoning by carbon monoxide formed during the coal gasification limited cell affordability, usefulness and lifetime. Consequently, interests on such electrochemical power sources dwindled.

In passing, it should be mentioned that Ostwald also recognized the importance of using batteries as energy storage devices when he declared [39]:

‘Another important thing is the question about accumulators, that is, about the best storage of electrical energy. We have to solve the problem of storing a maximum of energy in a preferably small room with low weight.’

He was so passionate about this idea that he named his house in Grossbothen, Germany, as ‘Landsitz Energie’, which means ‘energy cottage’.

Candidate fuel cell systems

The renaissance of the fuel cell concept can be attributed largely to the work of Tom Bacon [45]. He was an engineer by profession and thus appreciated the many potential advantages of the fuel cell over both the internal combustion engine and the steam turbine as a source of electrical power. Early in his career, Bacon elected to study the alkaline-electrolyte fuel cell, which used nickel-based electrodes, in the belief that platinum-group electrocatalysts would never become commercially viable. In addition, it was known that the oxygen electrode is more readily reversible in alkaline solution than in acid. This choice of electrolyte and electrodes necessitated operating the cell at moderate temperatures (100–200 °C) and high gas pressures. Bacon restricted himself to the use of pure hydrogen and oxygen as reactants. Eventually, in August 1959, he demonstrated a 40-cell system that could produce about 6 kW of power, which was sufficient to run a forklift truck and to operate a welding machine as well as a circular saw. His interest in fuel cells had, in fact, dated as far back as 1932 and he ploughed a lone furrow, with little support or backing. Bacon's enormous dedication to the challenge of developing practical cells is demonstrated by the following extracts from his Edgar Fahs Smith Memorial Lecture [46].

'In 1932, I happened to read an article in an engineering paper which described a scheme then being tried in Germany; the plan was to electrolyse water into hydrogen and oxygen at a pressure of 3–4000 lb in⁻², using cheap night power; the hydrogen was then to be transferred to a road vehicle where it would be stored in high tensile steel cylinders, and used in a modified internal combustion engine for propulsion; the oxygen could, if desired, be used instead of air in the engine, or else it would be sold. [...] I was at that time working in the development department of C. A. Parsons & Co. Ltd., in Newcastle-upon-Tyne, England; I had previously taken a degree in engineering at Cambridge University in 1925. [...] Having formulated some ideas, I sent in a report to the directors of the firm in 1937, drawing attention to the promising results already obtained with the hydrogen–oxygen cell and suggesting that the time was ripe for an attack on the problem, using high pressures, and moderate temperatures, and improved catalysts; [...] No action was taken by the directors, so not long after this, I sought advice from a well-known scientist, Sir Frank Smith. After listening to what I had to say, Sir Frank asked whether I had repeated Grove's experiments; I had to admit that I had not. He strongly advised me to

start some experimental work myself, so the next few years were spent first repeating some of the early work, and then trying a few simple ideas of my own. Some of this work was done in my own spare time at home, but I regret to say that, later on, much of it was done in the firm's time, when I should have been doing other things. [...] in 1939, a cell was built [...] which was made for me privately in the tool room at Parsons, cost me £30—quite a large amount in those days—but was cheap at the price. [...] I well remember the day when the managing director of the firm came round the works rather unexpectedly and approached the part of the building in which I was working; I had of course arranged a warning system in case this unfortunate eventuality should arise; the apparatus was quickly shut down, and I retired to a place of hiding. All went well, and I was not discovered; but I heard afterwards that he stood and looked at the apparatus for some time before passing on; not being very well qualified technically, he had mercifully shrunk from asking any awkward questions which might have exposed his own ignorance, but which would undoubtedly have caused my downfall. [...] A second report was sent in to the directors in January 1940, describing the work done with the pressure cell, and I could no longer conceal the fact that it had been done on the premises; this of course led to an ultimatum, and I was faced with the alternatives of a month's notice or giving the work up altogether. In view of the experience which I had now obtained, the latter course was unthinkable; [...] I was fortunate in obtaining an introduction to Dr. Charles Merz who [...] made arrangements for me to continue the work at King's College, University of London, in the summer of 1940, under the supervision of Professor A J Allmand, [...] He too was an outstanding personality; and he once told me that every year he had devoted one of his lectures to the subject of fuel cells, hoping to inspire one of his students to start work on this fascinating but difficult problem. He also gave me two warnings; the first was "You must always remember, Bacon, that electrochemistry is a partially understood subject"; and the second was "It will be a long trail". It would be difficult to question the wisdom of either of these remarks.'

A major opportunity to apply fuel cells arose in the early 1960s with the advent of space exploration. In the USA, fuel cells were first used to provide spacecraft power during the fifth mission of Project Gemini. Batteries had been employed for this purpose in the four earlier flights, as well as in those conducted in the preceding Project Mercury.

This switch in technology was undertaken because payload mass is a critical parameter for rocket-launched satellites and it was judged that fuel cells, complete with gas supplies, would weigh less than batteries. Moreover, the objective of Project Gemini was to evolve techniques for advanced space travel — notably, the extra-vehicular activity and the orbital manoeuvres (rendezvous, docking, etc.) required for the Moon landing planned in the following Project Apollo. Also, lunar flights demand a power source of longer duration.

A proton exchange membrane fuel cell system (v.i.) manufactured by the General Electric Company was adopted for the Gemini missions (two modules, each with a maximum power of about 1 kW), but this was replaced in Project Apollo by an alkaline fuel cell (AFC) of circulating electrolyte design, as pioneered by Bacon and developed by the Pratt and Whitney Aircraft Company (later the United Technologies Corporation) (Fig. 22a). Both types of system were fuelled by hydrogen and oxygen from cryogenic tanks. The AFC could supply 1.5 kW of continuous power and its in-flight performance during all 18 Apollo missions was exemplary. In the 1970s, International Fuel Cells (a division of United Technologies Corporation) produced an improved AFC for the Space Shuttle Orbiter that delivered eight times more power than the Apollo version and weighed 18 kg less (Fig. 22b). The system provided all of the electricity, as well as drinking water, when the Space Shuttle was in flight.

The success of fuel cells in the space programme stimulated their deployment in terrestrial applications. Convenience and economics dictate that on Earth it is generally necessary to use air rather than pure oxygen for the positive electrode reactant and this introduces some technical challenges [47].

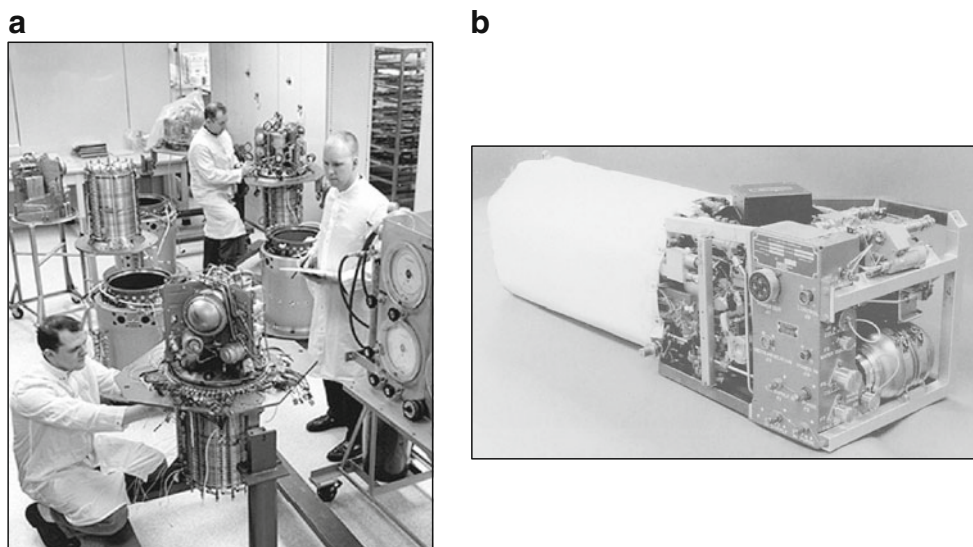
There are now six main types of fuel cell that can be broadly classified in terms of their temperature of operation, as follows:

- Low-temperature (50–150 °C): alkaline electrolyte (AFC), proton exchange membrane (PEMFC) and direct methanol (DMFC) fuel cells; the PEMFC is also known as the polymer electrolyte membrane fuel cell (but this results in same acronym, viz., PEMFC) and as the solid polymer electrolyte fuel cell (SPEFC).
- Medium-temperature (around 200 °C): phosphoric acid fuel cell (PAFC).
- High-temperature (600–1,000 °C): molten carbonate (MCFC) and solid oxide (SOFC) fuel cells.

Alcohols other than methanol have also been explored as potential fuels, e.g. ethanol, but comparatively little progress has yet been made with these alternatives. The generic term ‘direct alcohol fuel cell’ is often used to describe these systems. Remarkably, the century-old idea of Jacques [38] is being revisited in that attempts are being made to develop a direct carbon fuel cell through combining advances in MCFC and SOFC technologies; to date, only laboratory-scale tests have been conducted. Other exploratory systems include: biological fuel cells—also referred to as bioelectrochemical fuel cells, biofuel cells or microbial fuel cells—the direct borohydride fuel cell (a variant of the AFC), the formic acid fuel cell, the hydrogen–bromine fuel cell, and regenerative fuel cells (devices that can operate alternatively as an electrolyzer and a fuel cell, also known as reversible fuel cells).

The half-cell reactions of the above six types of fuel cell are summarized in Fig. 23a and key operational data are listed in Table 2. Apart from the DMFC, hydrogen is

Fig. 22 **a** Assembly of alkaline fuel cell modules for Project Apollo missions, **b** alkaline fuel cell module used in Space Shuttle Orbiter



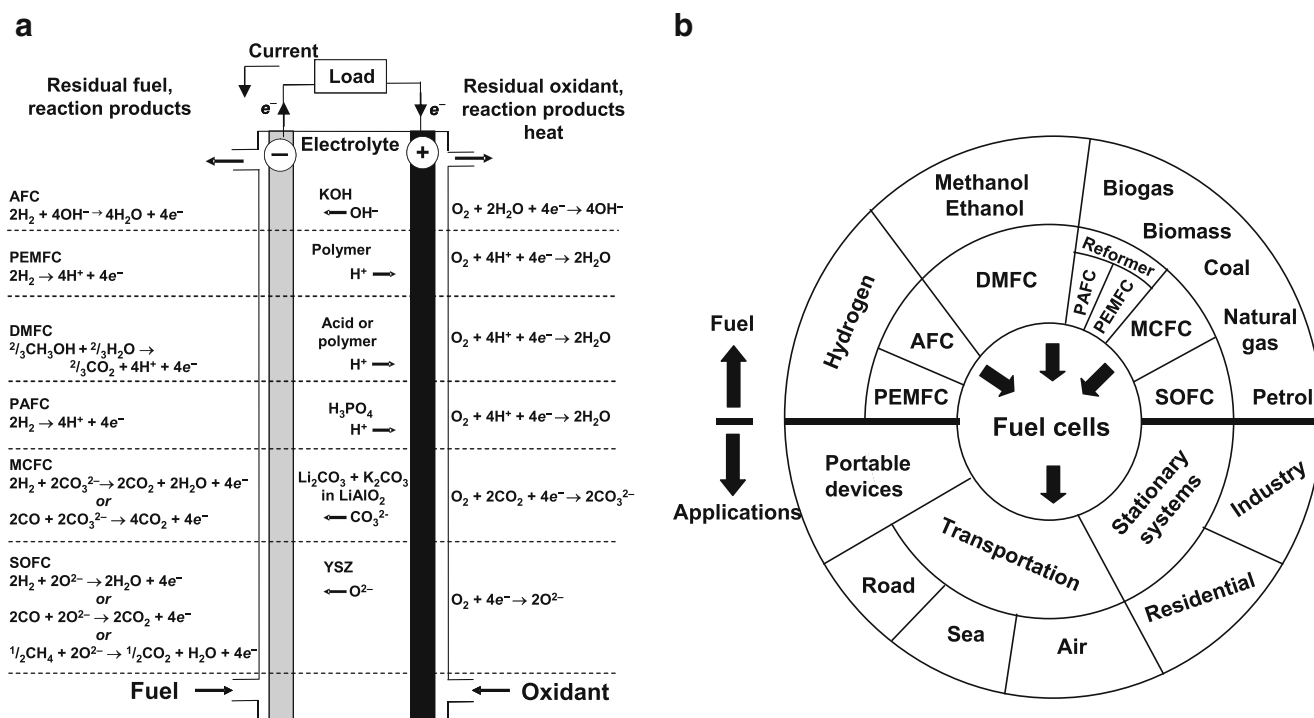


Fig. 23 a Electrochemical reactions occurring in different types of fuel cell [47], b fuels and applications for fuel cells

the preferred fuel on account of its high electrochemical activity. The AFC and the PEMFC are both demanding in terms of hydrogen purity; the gas must typically contain less than 10 ppm carbon monoxide. By contrast, the PAFC is somewhat more tolerant to carbon monoxide, whereas the high-temperature systems (MCFC and

SOFC) will accept carbon monoxide and a variety of hydrocarbon fuels. All of the designs require the fuel to be sulfur-free. A concise, visual summary of the fuels that might be used in different fuel cells, together with the various possible future applications for these devices, is given in Fig. 23b.

Table 2 Principal types of fuel cell

Fuel cell technology	Electrolyte	Temperature range (°C)	Electrocatalyst		Fuel	Efficiency ^a (% HHV)	Start-up time (h)
			Positive electrode	Negative electrode			
PAFC	H ₃ PO ₄	150–220	Pt supported on C	Pt supported on C	H ₂ (low S, low CO, tolerant to CO ₂)	35–45	1–4
AFC	KOH	50–150	NiO, Ag, or Au–Pt	Ni, steel, or Pt–Pd	Pure H ₂	45–60	<0.1
PEMFC	Polymer ^b	80–90	Pt supported on C	Pt supported on C	Pure H ₂	40–60	<0.1
DMFC	H ₂ SO ₄ Polymer ^b	60–90	Pt supported on C	Pt supported on C, or Pt–Ru	CH ₃ OH	35–40	<0.1
MCFC	Li ₂ CO ₃	600–700	Lithiated NiO	Sintered Ni–Cr and Ni–Al alloys	H ₂ , variety of hydrocarbon fuels (no S)	45–60	5–10
SOFC	Oxygen ion conductor	700–1,000	Sr-doped LaMnO ₃	Ni- or Co-doped YSZ cermet	Impure H ₂ , variety of hydrocarbon fuels	45–55	1–5

HHV higher heating value

^a The reported efficiency of a given type of fuel cell varies widely and often no information is provided on whether the higher heating value (HHV) or the lower heating value of the fuel is used. The efficiencies here have been taken from the literature should be treated with caution as to their exact meaning and they are simply included to provide an approximate comparison of the performance of the respective systems

^b Proton-conducting polymer: perfluoro-sulfonic acid polymer

The advantages of fuel cells over other generators of electrical energy such as gas turbines, steam turbines or internal combustion engines with alternators are as follows:

- Potentially high energy conversion efficiency over a range of sizes.
- Greater efficiency when operated at part-load, in contrast to engines.
- No moving components apart from auxiliary fans and blowers.
- Almost silent in operation.
- Flexibility of fuel supply.
- Very low exhaust emissions.
- Pure water emitted when using hydrogen as the fuel.
- Modular construction and ease of installation.

This impressive list of attributes has provided the incentive for much of the fuel cell research that has taken place in recent years. The six principal types of fuel cell have their own distinct characteristics and are at different stages in their development. Detailed information on these systems, as well as on those that are less advanced, may be found in the *Encyclopedia of Electrochemical Power Sources* [32].

Many of the challenges in realizing practical fuel cell systems centre on the requirement for low-cost materials that have a long operational life in the aggressive environments of the respective cells. Some types of fuel cell may fall by the wayside as, variously, their technical problems prove to be intractable, their reliability and lifespan inadequate and their costs unacceptable. Some systems may find niche markets that are of special importance to society, even if not contributing much to the overall energy/environment scene. Others may become influential in determining future energy policy throughout the world, as discussed below. There is still much to be done before all of the technical issues are settled, mass production lines are established and competitive products become available.

Electrochemical power sources—key agents for sustainability

There is serious concern over the sustainability of global energy supplies. Among the major drivers are:

- Climate change ('global warming'), ocean surface acidification and air pollution, which imply the need to control and reduce the anthropogenic emissions of greenhouse gases, especially emissions from the combustion of fossil fuels in transportation and thermal power stations.
- The diminishing reserves of oil and natural gas.

- The need for energy security adapted to each country, such as decreasing the dependence on fossil fuel imports from regions where there is political or economic instability.
- The expected growth in world population with the ever-increasing aspiration for an improved standard-of-living for all, particularly in developing and poor nations.

Various definitions of 'sustainability' exist in the literature, but they all convey the same message. The preferred definition is that formulated in 1987 by the World Commission on Environment and Development (the Brundtland Commission) which decided that sustainable development is a process that 'meets the needs of the present without compromising the ability of future generations to meet their own needs'[48]. In energy and environmental terms, this reduces to 'devising a set of energy technologies that meets humanity's needs on an indefinite basis without producing irreversible environmental effects' or, more simply, to 'substituting renewable forms of energy for fossil fuels'.

The major renewable sources of energy—or so-called renewables—are listed in Table 3, together with their method of utilization and the likely time-scale of early commercial adoption. In broad terms, the various forms have a number of attractive features. For instance, they:

- Enhance diversity in energy supply.
- Are secure, long-term, sustainable sources of energy.
- Reduce local and global atmospheric emissions.
- Open up energy supplies to rural areas and developing nations.
- Create new employment opportunities.
- Offer possibilities for the local manufacture of equipment.
- Conserve fossil fuels for use by future generations.

This is an impressive list of potential benefits, but for such benefits to be realized—both practically and on a large scale—it is essential that renewable forms of energy should become cost-competitive. This should eventuate gradually, as a result of technology refinement, economies-of-scale in utilization, and the imposition of taxes on conventional fuels in order to penalize the user for polluting the atmosphere.

Storage of renewable energy

Fossil fuels have two important characteristics in addition to being concentrated sources of energy, namely, they are energy stores and they are readily transportable. This means that the fuels may be stored until such time as they are required and may be transported by rail, road or pipeline to where they are to be used. By contrast, most of the renewables (except for biomass and hydro) cannot be stored and cannot be transported to the place of use, except by first

Table 3 Renewable energy sources and means of utilization

Energy source ^a	Energy utilization	Availability
Agriculture and forestry waste	Combustion process	Now
Energy crops	Combustion process	Now
Landfill and sewage gas	Combustion process	Now
Municipal solid waste	Combustion process	Now
Direct solar (active and passive)	Heating	Now
Geothermal	Heating/electricity	Now/limited scope
Hydro power	Electricity	Now
Wind power	Electricity	Now and developing
Hydrogen/fuel cells ^b	Electricity	Now and developing
Solar photovoltaic	Electricity	Now and developing
Tidal power	Electricity	Now/limited scope
Wave power	Electricity	Medium/long term
Solar–thermal	Electricity	Medium/long term

^a Although the distinction between ‘energy’ and ‘power’ is scientifically rigorous, in a general discussion of renewable energy sources there is a tendency to use the terms interchangeably. Nevertheless, it is preferable to use ‘energy’ where stored energy is implied (e.g. geothermal, biomass, hydrogen, batteries) and ‘power’ where a machine or device is rated in power output (e.g. hydro power, wind power, fuel cells)

^b Hydrogen is essentially a secondary form of energy but should be included as it is widely considered to be the ultimate conduit (the so-called hydrogen economy, v.i.) between the primary renewable source and its conversion to electricity, ideally via a fuel cell

converting them to electricity. Given that electricity is the most versatile and preferred form of energy for many applications, it is not surprising that renewable energy and electricity generation are so intimately bound together. Electricity is readily transmitted over long distances and distributed to consumers by cable but, when derived from renewables, there is the problem of matching the supply to meet the demand. For instance, wind turbines work well when the wind is blowing, but electricity is also required on windless days. Solar photovoltaic power is available during daylight hours, but much electricity consumption is at night. This calls for the development and application of systems for the efficient storage of electricity, and it is expected that indirect storage via the conversion to chemical energy in secondary batteries will play a leading role in future strategies to meet this critical need. An alternative means of storing renewable energy chemically is through the production of hydrogen, which may then be used to produce electricity in a fuel cell. Indeed hydrogen has come to be seen as the ‘ultimate’ fuel for the future (v.i.).

Generally, renewable energy facilities will be smaller than conventional power stations and will range in size from wind farms of a few megawatts capacity down to photovoltaic panels of a kilowatt or less. They will also be widely dispersed. The larger wind farms will feed into the electricity grid, but small wind turbines or photovoltaic arrays will supply power to communities such as farms, individual buildings, offices or shopping complexes. Battery storage for these so-called distributed electricity networks will be simpler than in the case of

the massive, megawatt-sized batteries required at power stations. Mains electricity may also be stored locally, near the point of use, in medium-sized batteries. Storing distributed electricity offers the advantage of load levelling the supply network, as well as the generating plant. This is especially beneficial in cities where the cost of installing additional cabling is high.

Solar photovoltaic power is particularly appropriate for medium-scale applications and is therefore more commonly implemented by means of stand-alone systems—known collectively as ‘remote-area power supply (RAPS) systems’—than by large-scale grid-connected plant. It should be noted, however, that small-scale systems are being increasingly used (even in cities and towns) as a cost-effective method of providing power to a wide variety of services, e.g. lighting, advertising signs, road traffic signals, parking ticket machines, uninterruptible power supplies, monitoring devices, railway signalling.

Secondary batteries have a number of features that make them well suited to storing photovoltaic electricity, namely:

- System input and output is in the form of low-voltage, direct-current electricity.
- Modular construction allows flexible sizing and easy battery exchange.
- Batteries respond immediately to supply and load variations and are very reliable in such duty.
- It is possible to match the internal resistance of the battery to that of the load for maximum power output.
- Batteries have a short lead time in manufacture.

The role of a battery in a RAPS system depends very much on the insolation level. In a tropical zone, there is little seasonal variation in this level, while in a desert region there is little rainfall and little cloud cover. Under these conditions, the insolation is fairly predictable and the function of the battery is usually to store electricity that is generated during the hours of daylight for use during the hours of darkness (so-called ‘supply levelling’). Only occasionally will there be the need to store more than a day’s worth of energy, so the extra margin of battery capacity required is quite small. The situation is different in temperate zones, in which there is typically a high incidence of cloud cover. Not only will it be necessary to have a much larger array because the insolation is low and erratic but also a considerable excess of battery capacity will have to be included to allow for several consecutive days of cloud cover. Superimposed on this is the seasonal variation at higher latitudes. Clearly, for a given application, both the array and the battery will be much larger and more expensive than the counterparts required for a RAPS system in a tropical zone.

A second role for the battery in a photovoltaic installation is to accommodate surges in power demand (i.e. ‘peak shaving’ operation). Power surges of relatively short duration and up to six times the steady load are common when appliances are turned on and off. Without a battery, it would be necessary to have a much larger array that is sufficient to meet the maximum instantaneous demand. This would be uneconomic. Similarly, when using an inverter to provide alternating current for domestic uses, inductive loads (such as motors in washing machines and vacuum cleaners, and compressors in refrigerators) all give rise to current surges of short duration. Both the battery and the inverter must be capable of meeting these instantaneous loads. While direct-current versions of some of these appliances are commercially available, as used in caravans and boats, they do tend to be more expensive.

Third, and finally, the battery is used to smooth the swings in current and voltage output from the array. Without this buffer function, the level of power fed to the load would be erratic. Thus, in addition to providing a diurnal storage capability—the primary role—the battery facilitates the matching of a fluctuating electricity supply to a fluctuating load.

Lead–acid batteries have invariably been chosen for wind or photovoltaic power supplies on account of their wide availability in a range of sizes and their acceptable cost. For the storage of renewable energy, the chief disadvantages of these batteries are the need for periodic water maintenance (except with valve-regulated cells), relatively poor performance at both low and high ambient temperatures, and a variable but limited cycle life. It should be noted, however, that research on valve-regulated batteries, particularly of the gel type, has resulted in marked improvements in life, notably

under the partial state-of-charge conditions that are typically experienced with renewable energy systems. The importance of the different limitations of lead–acid batteries will depend on the application, and it is necessary to weigh them carefully against the performance and cost of other battery chemistries.

Nickel–cadmium is the only other battery that is commercially available in sizes to suit large RAPS installations. The battery has high-rate and low-temperature performances that are better than those of lead–acid but, on the debit side, it is far more expensive and has a lower voltage (1.2 vs. 2 V). The higher cost may be acceptable for sites that are remote, unmanned and difficult to access, especially in polar latitudes where use of the battery will furnish savings in maintenance costs to be weighed against the greater capital outlay. Despite such possible advantages, nickel–cadmium batteries have fallen out of favour due to environmental concerns associated with the disposal of toxic cadmium in spent cells. Nickel–metal hydride batteries have replaced nickel–cadmium for many applications, but they are mostly confined to small cell sizes. Larger batteries have been made and, if the demand were there, they could undoubtedly be manufactured. The same situation exists with rechargeable lithium technology. For both of these battery chemistries, the present high cost is a major obstacle to scale-up. Vanadium redox and, to a lesser extent, mechanically rechargeable zinc–air are the only other batteries worthy of consideration, but neither is commercially available and whether or not they will prove practical for the storage of renewable energy is, yet again, a matter of overall system economics. The practical realization of new rechargeable batteries is notoriously protracted and costly. Unless the wind or photovoltaic industries can justify such an investment for themselves, they will ultimately have to depend on batteries that are developed and produced for other applications.

Electric and hybrid electric vehicles

Most geologists and petroleum engineers are of the opinion that the Earth’s ultimate reserves of petroleum that are economically recoverable are in the region of 2,000 billion barrels, of which over 40% has already been used. Moreover, it is claimed that 94% of all available oil has been discovered. Some large oil-producing regions (USA, North Sea) have passed their peak production rates and are in decline. If this is not serious enough, an even more alarming fact is that much of the remaining ‘conventional’ oil (over 60%) is concentrated in just five Middle Eastern countries: Saudi Arabia, Iraq, Kuwait, United Arab Emirates and Iran. New oilfields will probably be discovered, for instance, in the countries of the former USSR and/or off the coast of West Africa, but are unlikely to compare in size with those of the Middle East and will not significantly change the overall picture. It is true that Alberta

(Canada) and Venezuela have, respectively, vast reserves of ‘oil sands’ and heavy oil (bitumen) that can be mined and refined to petroleum. In principle, both resources are sufficiently extensive to replace much of the conventional oil supply, although at a considerably higher cost, not only in economical terms but also with respect to environmental impact.

The demand for petroleum will doubtlessly intensify as the developing countries aspire to Western-style mobility. For example, given the population sizes of China and India, it is clear that if just these two countries were to become fully mechanized their petroleum requirements would constitute a large fraction of present oil production. Clearly, this cannot happen in a sustainable energy future. Nevertheless, present indications strongly suggest that there will be a growing competition for oil—not in the distant future, but within the next decade. Many countries are therefore exploring strategies to safeguard oil security.

The relationship between oil availability and climate change should also be considered. The atmospheric concentration of carbon dioxide has risen from 280 to 300 parts per million (ppm) before the Industrial Revolution to its current level of around 390 ppm. During this period of 200–250 years, an immense quantity of coal has been burnt, as well as almost half of the conventional petroleum ever likely to be available. Global temperatures are said to have risen by around 0.7 °C during the past 100 years. Based on such observations, the combustion of all the remaining readily accessible oil will lead to a significant, but possibly not catastrophic, increase in the level of atmospheric carbon dioxide. What will happen then as the conventional supply of oil becomes restricted? An aggressive exploitation of the extensive oil sands of Alberta would lead to greatly increased emissions of carbon dioxide per tonne of oil produced. A major worry, however, is that much oil will one day be obtained from coal. Unless this can be done economically with capture and permanent storage (‘sequestration’) of the carbon dioxide, there will be an alarming increase in this and other atmospheric greenhouse gases. At the local level, energy use in motor vehicles has been a major contributor to the degradation of urban air quality. The exhaust pollutants include carbon monoxide (which displaces oxygen in the blood), nitrogen oxides (NO_x , which combine with water to form corrosive nitric acid) and unburnt hydrocarbons (which react with NO_x in the presence of sunlight to form ozone and, thereby, photochemical smog—a lung irritant). Improvements in vehicle exhaust catalysts, and in environmental regulations in many countries, have resulted in substantial declines in the levels of these pollutants in urban air, but any further reductions would of course be welcome.

The transportation sector is by far the largest consumer of the world’s oil production, essentially all by petrol and diesel engines. Transportation is therefore a particularly important sector of the economy in which to expedite the introduction of sustainable energy sources. The obvious approach is to switch to electric propulsion since electricity is the most direct way of utilizing renewable energy. There are five broad categories of electric and hybrid versions of passenger and goods vehicles as distinguished by the source of electrical power.

- Vehicles supplied directly by mains electricity—this category includes tramcars and trolleybuses, electric trains and urban metro systems. All of these, with the exception of trolleybuses, run on tracks.
- Diesel–electric traction in which a diesel engine drives a generator to supply electricity to a motor—this form of propulsion is employed mostly in large units such as railway locomotives and ships.
- Battery electric vehicles—these include cars, vans and buses for urban use, as well as small off-road units for various duties. Conventional submarines are also battery-powered when operating submerged.
- Hybrid electric vehicles (HEVs)—these have dual power sources, at least one of which is electric.
- Fuel cell vehicles (FCVs)—several automotive companies are exploring the use of fuel cells to provide the electricity for motive power.

The widespread adoption of vehicles powered wholly or in part by batteries for commuting and for deliveries in cities would make a significant contribution to improving urban air quality and reducing the consumption of oil. To the extent, though, that the electricity is generated by a fossil-fuelled plant, the beneficial impact on energy sustainability and carbon dioxide emissions will be minimal. The overall efficiency (defined as the traction energy at the wheels divided by the primary energy input of the fuel supplied to the oil refinery or electricity power station) is not very different for petrol-driven vehicles and electric vehicles, while with electric vehicles the emissions are merely transferred from the tailpipe to the power station. Thus, the contribution that battery electric vehicles might make to global energy sustainability is second-order, unless and until renewable sources of energy become the prime source of electricity.

Conventional internal-combustion-engined vehicles (ICEVs) are frequently designed for power rather than for economy. Consequently, the vehicles have engines that are too large and inefficient for steady driving so as to have power in reserve for acceleration and overtaking. The way to avoid this profligate waste of petroleum, and concomitantly reduce vehicle emissions, is to divorce steady-state performance from acceleration by having two separate

energy sources, i.e. one for cruising and one for power. For this reason, many car manufacturers are putting sizeable efforts into the development of the HEV concept. Hybrids are attractive not only to the automotive industry since a paradigm shift in technology is not required, but also to the users because such vehicles are reasonably cost-competitive with ICEVs and will deliver superior fuel economy. Nevertheless, for HEVs to achieve deep penetration into road transportation markets, a high-performance and low-cost battery must be developed.

The hybrid electric vehicles are of two basic types: the ‘series HEV’ and the ‘parallel HEV’, as illustrated schematically in Fig. 24a, b, respectively. In the series configuration, the output of a heat engine is converted to electrical energy through a generator which, either separately or jointly with a battery, powers a single drive-train. In one typical version, the series HEV would have a battery which is sufficiently large to meet the daily range and peak-power requirements for city driving and a small heat engine (internal combustion engine or gas turbine) to generate electricity purely as a ‘range extender’ for out-of-town driving. The battery is said to operate in the ‘dual-power mode’. The series HEV is essentially an electric vehicle with an EV-sized battery and a small auxiliary engine. By contrast, the parallel HEV has two distinct drive-trains such that the vehicle can be driven mechanically by a heat engine or electrically by a battery-powered motor, or by both. The heat engine is larger than that in a series HEV (but smaller than that in a conventional automobile) and is sized for steady highway driving. The independent battery system provides auxiliary power for acceleration and hill climbing, restarts the engine in city traffic and accepts regenerative braking energy (during deceleration or hill descent, the motor converts the potential energy of the vehicle into kinetic energy and puts charge back into the battery). In such duty, the battery has to furnish and absorb high, short bursts of current and is said to operate in the ‘power-assist mode’. The parallel HEV corresponds to a conventional automobile with a smaller engine and a larger battery.

A typical arrangement of the power-train components in a HEV is shown schematically in Fig. 24c. To date, most hybrids have been produced with a parallel configuration. In the final analysis, the choice of a hybrid system depends on the required duty cycle of the vehicle, the degree of engineering complexity, the capital and running costs, and the emission regulations that have to be observed.

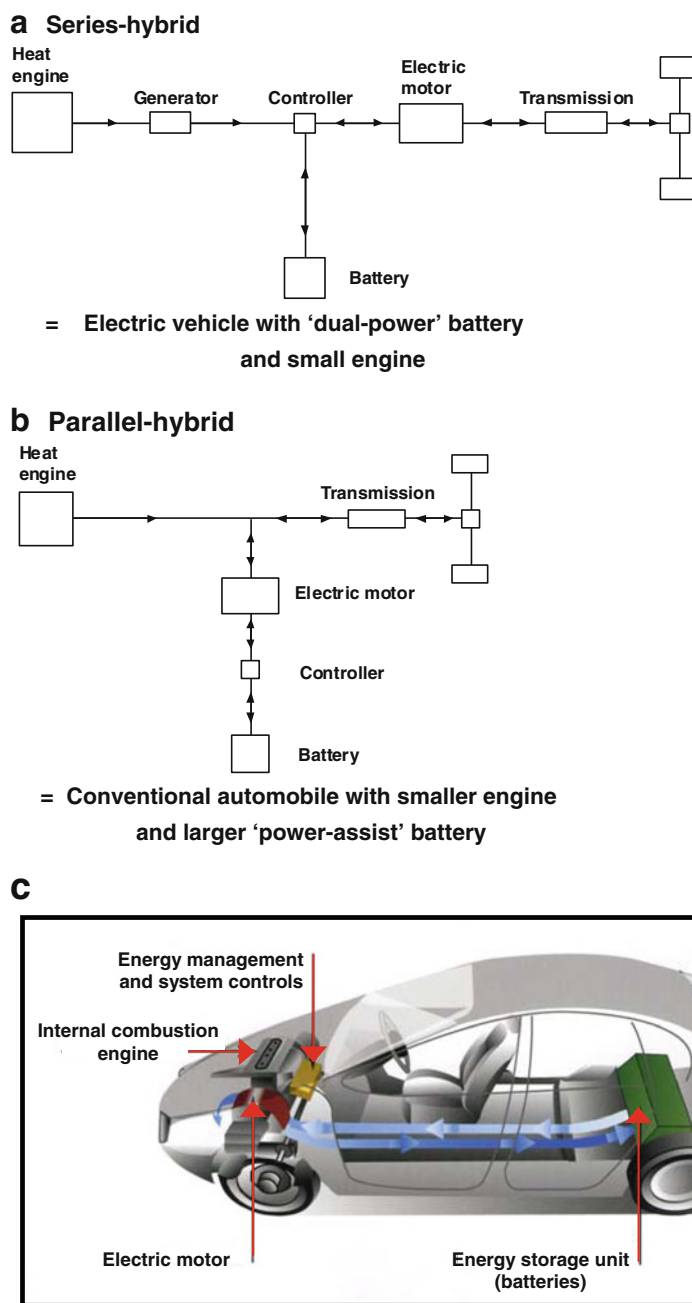
The design of an HEV is determined by the electricity flow between the battery pack, the internal combustion engine and the motor. For ‘micro-hybrids’, also known as ‘stop–start hybrids’, the battery pack is required to provide electricity to start the engine (at stop lights, rail crossings, etc.) and to receive electricity from the motor through regenerative braking. For ‘mild hybrids’ and ‘medium

hybrids’, in addition to engine starting and regenerative braking, the battery is required to supply electricity for acceleration. For ‘full hybrids’ and ‘plug-in hybrids’, the battery is further required to provide electricity for short distances of pure electric driving. The plug-in hybrid has a longer electric driving range than the full hybrid, and it has an on-board charger to replenish the battery pack when parked. All of the different types of HEVs demand the battery to be discharged and charged at high rates. A high-rate discharge is necessary for engine cranking and acceleration, while a high-rate charge is associated with regenerative braking.

The present HEVs are fitted with nickel–metal-hydride batteries; these provide adequate performance but are expensive. Progress is being made with rechargeable lithium batteries, but again there will be a cost penalty and there are also safety concerns. The valve-regulated lead–acid battery is the only other option and it offers great advantages in terms of low initial (capital) cost, a well-established manufacturing base, extensive distribution networks, and high efficiency in lead recycling. On the debit side, the running cost of the VRLA battery is expensive on account of its short service life. For HEV applications, the battery must be operated at high charge/discharge rates in a partial state-of-charge condition, namely, within a 30–70% state-of-charge (SoC) window. This is because the battery cannot supply the required cranking current when the SoC is below 30% and cannot accept charge efficiently either from regenerative braking or from engine charging when the SoC is above 70%. Overall, the VRLA battery in a HEV is subjected to high-rate partial-state-of-charge duty and fails prematurely owing to sulfation of the negative plates. A compact layer of ‘hard’ lead sulfate progressively builds up on the plates that are difficult to recharge and thereby promotes the early evolution of hydrogen which, in turn, lowers the charging efficiency [49]. Eventually, the accumulation of lead sulfate reduces the effective surface area to such an extent that the plate can no longer deliver/accept the power associated with engine cranking, acceleration and regenerative braking. To circumvent this problem, CSIRO has developed the valve-regulated UltraBattery™, which essentially protects negative plates from high-rate charge/discharge [50]. To understand the configuration and operating principles of this innovative device, it is first necessary to examine the basics of supercapacitor technology.

Supercapacitors differ from conventional electrostatic and electrolytic capacitors in that they store charge in the form of ions, rather than electrons, on the surfaces of materials with high specific areas ($\text{m}^2 \text{g}^{-1}$). In the ‘symmetric’ design (Fig. 25a), the electrodes are usually prepared as compacts of finely-divided porous carbon, which provide a much greater charge density than is possible with nonporous, planar electrodes. Supercapacitors

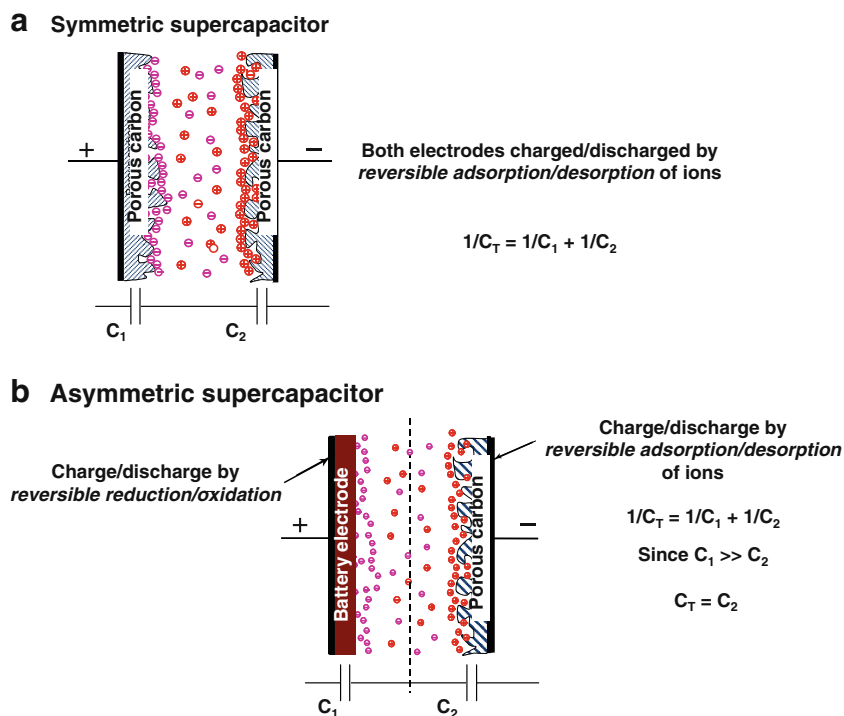
Fig. 24 **a, b** Series and parallel configurations of hybrid electric vehicles, **c** layout of power-train components



can store vastly more energy than conventional capacitors and much of the storage capacity is due to the charging and discharging of the electrical double layers that are formed at the electrode|electrolyte interfaces. The voltage is lower than for a conventional capacitor, while the time for charge and discharge is longer because ions move and reorientate more slowly than electrons. In these respects, the supercapacitor begins to take on some of the characteristics of a battery, although no electrochemical reactions are involved in the charge and the discharge processes. The 'asymmetric' design of the supercapacitor moves one step closer to a battery (Fig. 25b). Here, an electrode material with a large specific

surface area (i.e. carbon) is combined with a 'battery-like' material that can be reversibly oxidized and reduced over a wide potential range. The energy is stored both by ionic capacitance and by surface (and near-surface) redox processes that occur during charge and discharge. The latter are electrochemical reactions (i.e. Faradaic processes) in which surface ions are reduced and oxidized. This enhances the amount of stored energy; the capacitance is twice that of the symmetric counterpart, as shown in Fig. 25a, b. Moreover, because the ions are confined to surface layers, the redox reactions are rapid and are fully reversible for many thousands of times and this makes for a long cycle life.

Fig. 25 Schematic representation of **a** symmetric and **b** asymmetric supercapacitor. The asymmetric design has twice the capacitance of the symmetric design



The CSIRO valve-regulated UltraBattery™ combines a VRLA battery with an asymmetric supercapacitor into a single unit without the need for extra electronic control. The hybrid structure is illustrated schematically in Fig. 26a. A VRLA cell, which has one lead dioxide positive plate and one lead negative plate, is combined with an asymmetric supercapacitor, which is composed of one lead dioxide positive plate and one carbon-based negative plate (i.e. a capacitor electrode). Since the positive plates in the VRLA cell and the asymmetric supercapacitor have the same composition, they can be integrated into one unit by connecting internally the capacitor electrode and the VRLA negative plate in parallel. These two electrodes now share the same positive plate. With this design, the total discharge or charge current of the combined negative plate is composed of two components, namely, the capacitor current and the VRLA negative-plate current. The capacitor electrode can now act as a buffer to share current with the negative plate and thus prevent it from being discharged and charged at high rates.

A pack of prototype batteries, constructed by the Furukawa Battery Co., Ltd., in Japan, were fitted to a Honda *Insight* HEV and successfully completed a 160,000-km (100,000 miles) test under at the Milbrook Proving Ground in the UK [50] (Fig. 26c, d). The battery pack demonstrated very good acceptance of charge from regenerative braking (even at 70% SoC), exceeded the power requirements specified in the US FreedomCAR protocol [51], and remained in an excellent condition. The UltraBattery™ can be readily manufactured in a conventional

lead–acid factory and is therefore highly cost-effective; it is only 20–40% of the cost of the nickel–metal–hydride counterpart. The device is particularly suited to micro-hybrids since these vehicles do not require an excessive amount of energy for power-assist. Micro-hybrids have become a popular option in Europe and are slated to make a deeper impact globally in the near future.

Mass production of the UltraBattery™ is now in progress in Japan and the USA; a specimen unit is shown in Fig. 26b. The USA government has awarded US\$32.5 million dollars towards ongoing development. The grant was announced by President Obama on 5 August 2009 as part of US\$2.4 billion in funding for 48 advanced battery and electric-drive projects under the American Recovery and Reinvestment Act. The UltraBattery™ is also a promising technology for the storage of electricity obtained from wind turbines and photovoltaic arrays. CSIRO is presently exploring such applications.

The fuel cell vehicle operating on hydrogen, most probably with a proton-exchange membrane fuel cell, is seen by many as the ultimate solution to the increasing energy security and environmental problems that confront road transportation. As discussed below, hydrogen can be liberated from a wide range of primary feedstocks, even from cheap coal of which the world has prodigious quantities. Such vehicles would therefore release coal-rich nations from the costs and political uncertainties of importing petroleum. The appeal of FCVs to manufacturers is less obvious. At their present stage of development, PEMFC power systems are hugely more expensive than

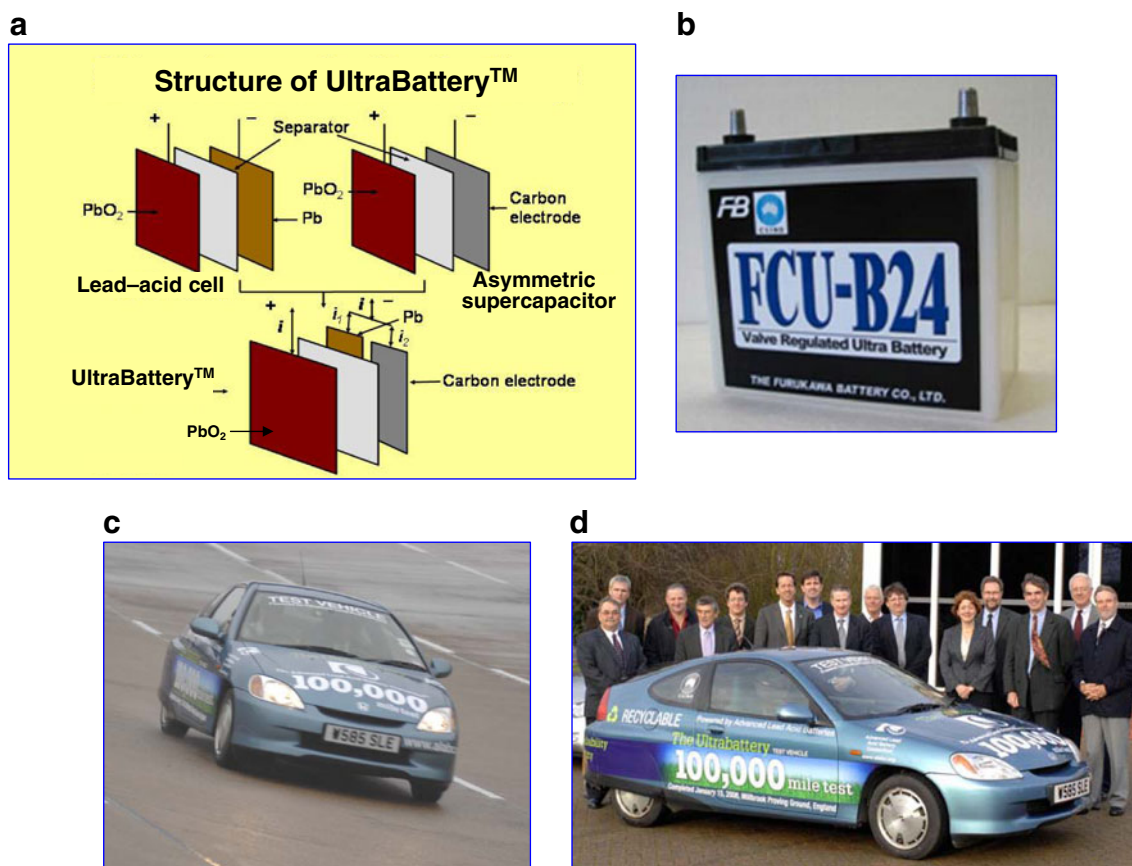


Fig. 26 **a** Schematic representation of UltraBattery™ configuration and operation; **b** UltraBattery™ designed for HEV applications; **c** Honda Insight HEV equipped with UltraBattery™ pack undergoing field trials at Millbrook Proving Ground, UK; **d** inspection of test

vehicle by staff from the US Senate Energy and Natural Resources Committee and from member companies of the Advanced Lead-Acid Battery Consortium

ICEs (up to 60 times greater per kilowatt produced) and the ability to reduce the costs to a competitive value must be questionable. In addition, numerous other technical difficulties have to be resolved before FCVs can become commercially viable. Above all, there are over-riding problems of where to produce the hydrogen, how to convey it to the vehicle refuelling sites, and how to store it on board.

The efficiency of fuel cells (the fraction of the fuel's energy converted into useful output) is also a critical issue. Much is still made of the fact that fuel cells are not heat engines like ICEVs so that their efficiency is not limited by the Carnot cycle and accordingly must be high by comparison. This reasoning promotes interest and investment in fuel cell technology. The thermodynamic 'theoretical' efficiency, defined as the ratio of reaction-free energy to enthalpy, can be above 80% [52]. Nevertheless, the electrochemical kinetic theory says that this ratio is an upper limit that is only reached at equilibrium when the current is zero. In practice, the efficiency must be smaller. How much smaller is difficult to calculate and depends on numerous kinetic and other parameters such as over-

potential and ohmic losses, the occurrence of side reactions, fuel loss via the electrolyte, partial fuel usage and energy consumption by the auxiliary components. These factors have a 'theoretical' basis just as sound as the thermodynamic analysis of fuel cell efficiency. They cannot be dismissed as temporary practical impediments that are simply waiting to be overcome by further development.

Despite such serious barriers to success, an appreciable investment in FCVs is in place in Europe, Japan and the USA. Emphasis has been on the production of urban buses and private cars; all are employing PEMFC systems. Although notable improvements have been achieved in the performance of PEMFC stacks for road transportation applications, the greatest problem is still that of cost. This must be reduced substantially if FCVs are to come into general use. Nonetheless, there is a strong argument that the research should continue given the ultimate achievement of a state of nirvana, in which road transportation is provided by affordable and reliable FCVs that operate on hydrogen derived from water by electrolysis with electricity generated from renewable energy sources. This would constitute a

global transportation system that is truly sustainable, i.e. one that is supported by abundant energy supplies and has no environmental impact. Such a prospect raises the question of whether hydrogen has the potential to occupy a major position in the future world energy scene. Therefore, it is timely to close this examination of the past, present and future usefulness of electrochemical power sources in the conversion and storage of energy, obtained either from fossil fuels or renewable sources, with a brief examination of their expected role in a proposed hydrogen society.

A transition to a hydrogen economy?

Hydrogen is being promoted worldwide as a panacea for energy problems in that it may eventually replace, or at least greatly reduce, the reliance on fossil fuels and that, obviously, as a carbon-free fuel its use would not give rise to carbon dioxide emissions [53]. Although it is the most abundant element in the universe—the stuff from which stars are made—hydrogen does not occur freely on earth but is predominantly found in combination with oxygen as water and with carbon as fossil fuels. Chemical, thermal or electrical energy has to be expended to extract hydrogen from these sources. Hydrogen is therefore not a new form of primary energy but a vector (or carrier) for storing and transporting energy from any one of a myriad of sources to where it may be utilized. In this respect, it is analogous to electricity, which is also a secondary form of energy. Hydrogen and electricity are complementary: electricity is used for a multitude of applications for which hydrogen is not suitable, whereas hydrogen, unlike electricity, has the attributes of being both a fuel and an energy store. These two energy vectors are, in principle, interconvertible: electricity may be used to generate hydrogen by the electrolysis of water, while hydrogen may be converted to electricity by means of a fuel cell. In fact, the fuel cell is the key enabling technology for the widespread adoption of hydrogen energy.

Specifically, hydrogen has the following attributes:

- It can be derived from fossil and non-fossil sources (renewable or nuclear energy).
- It can serve as an alternative fuel for internal combustion engines.
- It is ideal for use in fuel cells for transportation and for distributed energy supply.
- It is oxidized cleanly to water with no emissions of greenhouse gases; when captured from water using renewable energy, the fuel cycle is closed and no pollutants are released in the overall process.

The proposal to use hydrogen as both an energy vector and a sustainable fuel has become known as the ‘hydrogen

economy’; the overall scheme is illustrated conceptually in Fig. 27. The upper part of the diagram is generally referred to as the transitional phase, during which hydrogen is produced from fossil fuels; the lower part relates to the long-term, post-fossil fuel age when hydrogen will be manufactured from renewable energy sources and used both as a storage medium and as a superclean fuel. Not unexpectedly, the building of a hydrogen economy presents great scientific and technological challenges in production, delivery, storage, conversion and end-use. In addition, there are many policy, regulatory, economic, financial, investment, environmental and safety questions to be addressed.

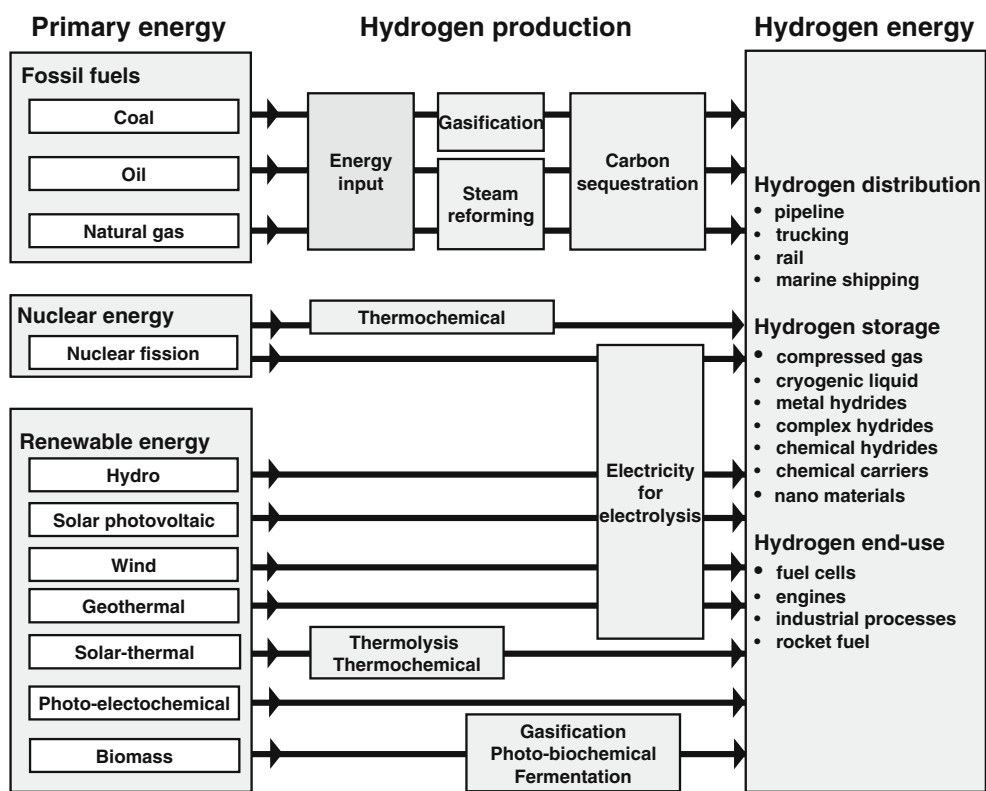
There is, however, a fundamental problem with the concept of a *sustainable* hydrogen economy. Within our present span of vision, renewable energy sources alone do not afford a path to a carbon-free future because not only are they difficult to harvest on a large scale but also breakthroughs in cost must be achieved if they are to supplant fossil fuels and become commonplace. Also, there is often local opposition to the construction of renewable facilities such as hydroelectric dams or wind farms, which may spoil areas of scenic beauty or interfere with natural habitats. The counter-proposition of increasing the deployment of nuclear power, which is not usually regarded as renewable energy but at least is carbon-free, is unpopular in many quarters because of concerns over radioactive waste.

Hydrogen production

To date, the prime uses of hydrogen have been in the petroleum industry for the refining and upgrading of crude petroleum, and in the chemical industry for the manufacture of ammonia (e.g. for fertilizers), methanol and a variety of organic chemicals. Other important applications are found in the food industry for the hydrogenation of edible plant oils to fats (margarine) and in the plastics industry for making various polymers. Lesser amounts are consumed in the metals, electronics, glass, electric power and space industries. Very little hydrogen is utilized as a fuel.

The various primary energy sources from which hydrogen can be produced and the potential uses for this energy vector are summarized schematically in Fig. 28 [54]. In the near term, it is probable that hydrogen will, as now, be derived largely from fossil fuels since this is the most economic route. At present, the world production of hydrogen is around 45–50 Mt per year. Most of this is extracted from natural gas by steam reforming; the remainder is acquired principally from oil and coal by partial oxidation processes. Solar–thermal reforming of natural gas is an interesting future prospect but has yet to be fully demonstrated. Unfortunately, all of these methods involve a concomitant release of carbon dioxide and thus, for a sustainable future, they require the development of

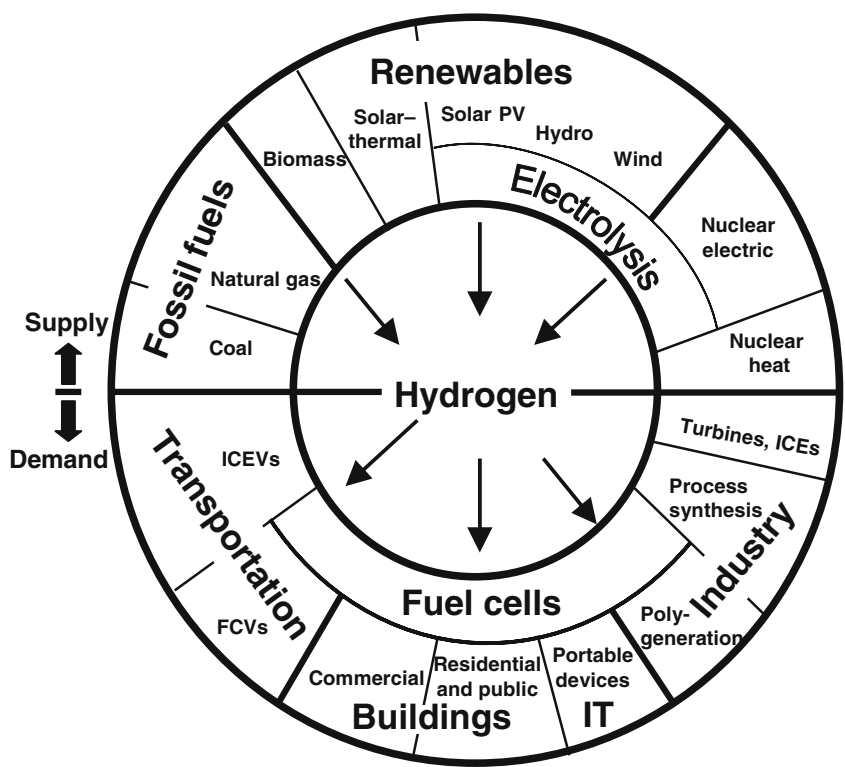
Fig. 27 A sustainable hydrogen economy [53]



practical technologies for the sequestration of the gas. Of course, if the primary concern is that of security of fuel for use in road transportation and the aim is to substitute hydrogen for petroleum, then the emissions problem will

become more manageable. Plasma reforming of natural gas is attractive in that solid carbon is formed rather than carbon dioxide. The drawbacks are that the process requires substantial amounts of electricity and, obviously, no advan-

Fig. 28 Hydrogen supply options and potential major uses [54]. PV photovoltaic (cells), ICEs internal combustion engines, IT information technology, FCVs fuel cell (electric) vehicles, ICEVs internal-combustion-engined vehicles



tage is taken of the energy that, otherwise, would have been obtained from the combustion of carbon. In terms of energy efficiency, therefore, it does not appear to be a very promising option. The manufacture of hydrogen from dry biomass by gasification is perfectly feasible. Moreover, given that the process is deemed to be ‘carbon neutral’, direct combustion can be employed with no need to capture the carbon dioxide. The size of the operation is generally restricted by the quantity of material that can be harvested and collected close to the processing plant. This is because biomass is not dense and generally cannot be conveyed economically by road over distances of more than 100–200 km. The bacterial fermentation of wet biomass can be made to yield biogas, which contains a moderately high percentage of hydrogen, but this line of investigation is still in its infancy.

Water is a huge storeroom of hydrogen, but energy is required to split this resource into its component elements. Only 4% of the hydrogen worldwide is generated by electrolysis, invariably when there are special reasons that make this route economic, e.g. where there is a surfeit of cheap hydroelectricity or when the hydrogen is a by-product of the chlor-alkali process for the manufacture of chlorine and caustic soda. Bulk production of hydrogen via electrolysis appears improbable until renewable or nuclear electricity becomes widely available and considerably cheaper than at present. The main attribute of electrolytic hydrogen is its ultra purity, which is an important requirement for proton exchange membrane fuel cells, *v.s.* Nevertheless, the use of valuable electricity to electrolyze water and then feeding the resultant hydrogen to a fuel cell is intrinsically wasteful by virtue of the combined inefficiencies of the two devices involved. This really only makes sense in situations where there is more electricity than can be consumed as such or where there are strong reasons for wanting hydrogen that transcend considerations of efficiency and cost. One situation might be on islands or in isolated communities where there is plenty of renewable energy in the form of wind or photovoltaic electricity but no means of storing it from times of surplus to times of peak demand. Hydrogen could then provide an energy store and later be reconverted to electricity, although this approach to storage would be in competition with batteries or standby diesel generators. Other opportunities lie in countries like Norway or Iceland where there is a surplus of cheap hydrothermal or geothermal electricity.

The several ways in which solar energy may be employed to split water are summarized in Fig. 29. Thermochemical cycles have been studied for many years, with new cycles emerging periodically. Very few, however, have been taken beyond the laboratory stage. Some scientists link this technology to high-temperature nuclear reactors for the provision of the necessary heat input, others to solar–thermal towers. High-temperature nuclear reactors are not yet available but would be of such a

size that considerable quantities of heat would be liberated. This, in turn, would entail the construction of a correspondingly large engineering plant to undertake the thermochemical processes. Solar–thermal towers, by contrast, would have a much lower heat output but still sufficient for hydrogen production via thermolysis. Nevertheless, the commercial viability of undertaking these two processes on a relatively small scale must be questionable. It is doubtful whether either approach will find major application in the near term.

Apart from the direct use of photovoltaic electricity for electrolysis, the other solar-based methods for extracting hydrogen from water, namely, via photo-electrochemical or photo-biochemical reactions, are either limited in scope or at too an early stage of development to predict the outcome. It would appear, therefore, that there is a long road ahead before electrolytic hydrogen from a solar source becomes competitive with hydrogen from conventional fuels. Nevertheless, there are many avenues of electrochemistry, materials science and catalysis to be explored and time in which to conduct this fundamental research, while renewable energy sources are being harnessed to an ever-growing extent.

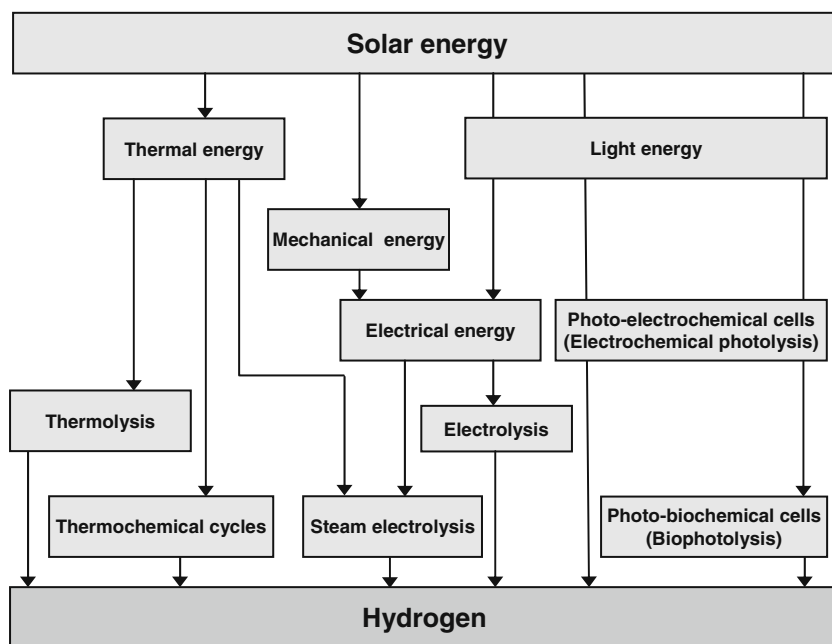
Hydrogen distribution and storage

To be useful as a future fuel, hydrogen has to be conveyed to the point of use and stored there until required. The distribution and storage of hydrogen are intricately bound together and depend on both the scale of operations and the intended application. In general, the storage of hydrogen for stationary energy supplies is less demanding than for transportation systems, where there are more severe constraints in terms of acceptable mass and volume, speed of charge/discharge and heat dissipation. Finding a satisfactory solution for the on-board containment of hydrogen is one of the great challenges facing the development of fuel cell vehicles.

In the gaseous state, the most obvious method for distributing hydrogen would appear to be via pipeline. Indeed this has long been the practice in both refineries and industrial chemical plants. The transmission of hydrogen as a universal energy vector, however, is a more difficult proposition since the distances would be much greater and the allowable costs much less. Apart from the massive capital investment that would be required, there are many technical issues such as materials compatibility if an existing natural gas infrastructure is to be used, pipeline integrity, leak minimization and high compression costs. As with natural gas transmission systems, the pipelines themselves would provide some degree of storage for hydrogen. Large-scale containment underground in natural or anthropogenic cavities is also a possibility.

On a much smaller scale, steel cylinders are used for the storage of gaseous hydrogen at pressures of up to

Fig. 29 Solar-to-hydrogen conversion options



80 MPa. For portable and mobile applications, cylinder weight and volume must obviously be minimized. To some extent, this requirement has been achieved by using all-composite vessels composed of carbon-fibre shells with aluminium liners. Liquid hydrogen (LH₂) is a more attractive storage medium as its density is 850 times greater than that of the gaseous form. The delivery of larger amounts of hydrogen as a cryogenic liquid (LH₂) is perfectly possible and also offers short-term storage. The problems with LH₂ are the capital cost of the liquefaction and storage plant, the substantial input of electrical energy required to liquefy the gas and the losses due to ‘boil-off’ during transfer and on standing. Distribution via LH₂ has been proposed and demonstrated for use in hydrogen-fuelled vehicles, but a question mark remains over the practicality and safety of permitting members of the public to refuel their own cars. Given this concern, compressed gas in cylinders has been adopted by most developers of fuel cell vehicles, regardless of the fact that space is generally at a premium.

Certain metals and alloys can repeatedly absorb and release hydrogen under moderate pressures and temperatures via the formation of hydrides, i.e.:



Heat must be removed during absorption of the hydrogen but has to be added to effect desorption.

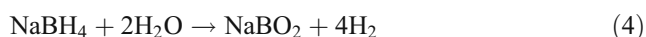
Hydrides have relatively poor mass storage for hydrogen, namely, from 1 to 2 wt.% for materials such as CaNi₅H₄ that operate at near-ambient temperatures up to

3.6 wt.% for magnesium-based materials such as Mg₂NiH₄ that function above 300 °C. By contrast, hydrides have a relatively good theoretical volumetric performance of 0.1 kg dm⁻³. Since lower-temperature materials would be preferred in most cases, the challenge is to develop new alloying techniques that increase the gravimetric density of the hydrides. Other drawbacks with metal hydride storage include excessive mass, high cost and very slow refuelling due to the time required to dissipate the heat produced during the hydriding reaction.

Certain organic chemicals contain significant atomic proportions of hydrogen that can be recovered and thus may be considered as prospective hydrogen carriers. One of the best known of these is cyclohexane (C₆H₁₂), which can be decomposed catalytically to give benzene (C₆H₆) and hydrogen. The hydrogen content is 7.1 wt.%. This is an example of a reversible (round-trip) carrier since cyclohexane is manufactured by the hydrogen reduction of benzene over a nickel catalyst at 150–200 °C. Liquid ammonia (NH₃), hydrazine hydrate (N₂H₄·H₂O) and ammonia borane (NH₃BH₃) will theoretically store 17.7, 8.0 and 12 wt.% H₂, respectively. In practice, however, these three materials present many safety and operational difficulties, especially when the hydrogen is intended for use in vehicles.

Hydrogen may be stored chemically in the form of ionic salts that are composed of sodium, aluminium or boron and hydrogen—the so-called complex chemical hydrides. The alanates Na[AlH₄] and Na₃[AlH₆] have been widely studied. Thermal decomposition of Na[AlH₄] to discharge hydrogen takes place at temperatures up to 180 °C. Sodium

borohydride, NaBH_4 , is stable up to about 400 °C and is therefore not suitable for providing hydrogen through a thermal activation process. It does, however, deliver hydrogen on reaction with water, i.e.:



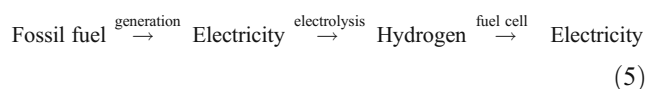
This is an irreversible reaction. Based on the mass of NaBH_4 , the hydrogen released is 21 wt.%—a remarkably high output—but in practice the performance is lowered to around 7 wt.% when the weight of the total system is taken into account. Several similar hydrides are being evaluated for their reactivity with water, but they all suffer from the disadvantage that the storage of hydrogen is not rechargeable; the spent solution has to be returned to a processing plant for regeneration of the hydride. In road transportation applications, there may also be difficulties in controlling the reaction so as to evolve hydrogen at the variable rate set by the driving schedule of a given vehicle.

Considerable research is being carried out on materials that have structural elements with dimensions in the nanoscale range and thereby have high specific surface-areas ($\text{m}^2 \text{g}^{-1}$). Amongst these materials, it has been found that carbon and boron nitride nanostructures, clathrates and metal–organic frameworks can store hydrogen in the molecular state via weak molecular–surface interactions. Carbon nanotubes were some of the first nanomaterials to be investigated for hydrogen storage and many have been reported with capacities of several weight percentages that may be further enhanced by various pretreatments. There continues, however, to be considerable controversy over such findings because of the difficulty in preparing homogeneous, well-defined, pure and reproducible samples. Moreover, contrary to expectations, significant hydrogen storage in these materials usually requires either high pressure ($> 10 \text{ MPa}$) or low temperature (at least $-100 \text{ }^\circ\text{C}$).

Fuel cells—the enabling technology

Most types of fuel cell run on hydrogen at a level of purity that differs according to the specific system under consideration (v.s.). For localized electricity generation, hydrogen is converted into electricity (together with some heat) in a fuel cell, whereas for large-scale operations a gas turbine would be employed. Stationary fuel cells are seen as clean and quiet sources of electricity for dispersed generation. It is often claimed that they are efficient at converting hydrogen into electricity, although in fact only about 45% of the original electrical energy used to obtain the hydrogen by electrolysis, for example, may be recovered in stationary and mobile applications. This decline in performance arises from losses both in the electrolyzer and in the fuel cell itself. Indeed an efficiency of 45% is optimistic since it

takes no account of the losses incurred in compressing and distributing the hydrogen. When these are considered, along with the losses in generating the electricity in the first place, the efficiency for the overall process:



is likely to be under 20%. Energy efficiency is not, however, the sole criterion on which to judge fuel cells. The concept of distributed power generation without release of carbon dioxide is attractive, especially when part of a ‘combined heat and power’ scheme, but this is then dependent on the delivery of hydrogen from a central production facility that practices sequestration of carbon dioxide. The use of hydrogen fuel cells to propel electric vehicles is another situation where convenience outweighs inefficiency. Here the application is motivated primarily by the petroleum supply and security issue, as well as by concerns over atmospheric pollution in urban environments and global carbon emissions.

The future of hydrogen energy and that of the fuel cell are closely linked. Although the precise role for hydrogen has yet to be established, there are many reasons why hydrogen energy is stimulating worldwide interest. The exceptionally desirable features are its complementarity to electricity as an energy vector and its potential use as an energy store. Much depends upon future political and economic factors that are difficult to forecast, so hydrogen energy is usually viewed as a long-term option. If oil and gas supplies are restricted or even disrupted, if climate change is as severe as many fear and if there is a breakthrough in lowering the cost of renewable energy, then, quite suddenly, a transition to hydrogen energy could become highly attractive. Both the development of hydrogen technology and the establishment of an infrastructure will, however, be neither quick nor easy and this provides the justification for undertaking the basic science and engineering sooner rather than later—particularly with respect to the availability of more reliable, more durable and less-expensive fuel cells.

Postscript

The major objective for the energy industry—in all its sectors—is to develop procedures so that the present burgeoning demand for energy can be tolerated without exhaustion of the world’s resources and without further deterioration of the global ecosystem. Coal is the world’s largest reserve of fossil fuel and, in the years ahead, will be exploited aggressively by countries that have significant deposits, but no oil or gas, in order to achieve energy

independence. This raises the question of how best to utilize coal as a modern, clean energy source. Growth in demand suggests that electricity generation will be the prime market. Meanwhile, renewable sources of energy—especially wind and solar photovoltaic—will play an expanding, but still secondary, role in electricity generation. Thus, with its attributes of cleanliness and versatility, electricity is widely expected to assume a greater share of the overall energy market. The means to produce and manage electricity were first given to the world by Volta, Davy, Faraday, Grove and Planté. Now, as hopefully demonstrated by this brief survey of the world energy/environment scene, there are good reasons to conclude that the future well-being of the planet Earth may again lie in the hands of those who practise the science of electrochemistry, even if hydrogen ultimately becomes a universal energy vector. In my opinion, taking the electrochemical road to sustainability is a fascinating journey that should inspire all those who seek a clean and secure future for mankind.

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