

First there was hydrogen

Wojciech Grochala describes how the oldest, lightest and most abundant element in the universe continues to play an essential role on today's Earth.

The history of hydrogen — the element that fills the world as we know it — consists of a most dramatic set of events. Hydrogen and helium atoms emerged a measly 379,000 years after the Big Bang. As the hot, dense plasma of protons, electrons and photons that was the universe began to cool and expand, electrons and protons gathered to form atoms. Four hundred million years later stars — such as our very own Sun — evolved from gravitationally collapsed clouds of hydrogen gas, providing the heat necessary to sustain life in an otherwise giant, freezing, cosmic abyss at 2.7 kelvin. The third colossal breakthrough in hydrogen history came some 4.4 billion years ago, when the temperature on Earth dropped below 100 °C and dihydrogen oxide began to condense at its surface, allowing the emergence of life in the new aqueous environment.

Today hydrogen is estimated to account for 90% of all atoms in the universe, and it is essential to the material world. That includes ourselves: close to two-thirds of the atoms in our bodies are hydrogen. By no means an unproductive mass, the first element of the periodic table makes for an excellent chemical fuel — one that has been attracting increasing attention. The early Earth's atmosphere was rich in hydrogen, and bacterial enzymes called hydrogenases evolved to generate energy from molecular H₂ or H₂O (ref. 1). Microorganisms proliferated under reducing conditions, and many of those have survived on hydrogen fuel to this day.

Van Helmont was the first to find out that although hydrogen was combustible in air, it could not support combustion by itself. In 1671 Robert Boyle described the formation of gas bubbles from the reaction of iron filings with acid, but it was Cavendish who recognized H₂ (which he referred to as 'inflammable air') as a substance distinct from other gases, which, when it was burnt in 'dephlogisticated air' (oxygen) produced water. This discovery inspired Lavoisier



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to call the substance 'hydro-gen', meaning water-former, in 1783. Conversely, in 1800 Nicholson and Carlisle (shortly followed by Ritter) managed to decompose water into its elemental constituents using electrolysis. It is this process that we try to achieve today, although with a much smaller electric bill, through a photochemical process². The evolved H₂ gas is an excellent, ultra-light energy carrier, and very promising as a fuel — abundant and environmentally friendly as its oxidation produces water. Molecular H₂ filled one of the first balloons used to carry people in 1783 (pictured), and the fuel tanks of rockets two centuries later, permitting the inquisitive to explore further and further.

For practical applications, however, it must be stored in either a compressed, liquefied or solid state³. In 1970 in the Philips Research laboratories it was accidentally discovered that hydrogen could be reversibly taken up by intermetallic compounds in the form of a hydride⁴. This led to spectacular success for electrochemical hydrogen storage, and the first mass-produced nickel-metal-hydride battery-powered vehicles hit the roads of Japan in 1997. Together with vigorous development of hydrogen-oxygen fuel cells and solid proton conductors⁵, these advances bring us closer to fulfilling Jules Verne's dream that "hydrogen and oxygen ... will

furnish an inexhaustible source of heat and light", mentioned in *The Mysterious Island* as early as 1874.

Because H and H₂ constitute the prototypical atom and molecule, respectively, they have been extensively used by theoreticians for over a century — since the birth of quantum mechanics. These two species have served as test beds for rigorous critical evaluations of diverse quantum mechanical models and approximations⁶. The oxidation states of hydrogen span from -1 (hydride), through 0 (elemental), to +1 (proton), with very different physicochemical properties for each species. The H₂ molecule — isoelectronic to the closed-shell He atom in the unified atom model — is quite inert. It was only in 1984 that Kubas described the coordination of molecular H₂ to transition metals⁷. On the contrary, the H⁻ anion is a very strong base and a strong reducing agent, whereas H⁺ is a voracious acid and a powerful oxidizer; non (or very slightly)-hydrated protons present in a superacidic environment readily convert alkanes into carbocations⁸. Indeed, hydrogen has been a key element in establishing quite reasonable theories of acidity and basicity, which came to be viewed as proton transfer reactions in the Brønsted-Lowry theory.

The first element has never ceased to be of prime importance to many aspects of our world, and this is poised to continue with its major role in sustainable energy strategies. □

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Corrected after print 18 March 2015

H

He

Li

Be

B

C

N

O

F

Ne

Na

Mg

Al

Si

P

S

Cl

Ar

Correction

In the In Your Element article 'First there was hydrogen' (*Nature Chem.* **7**, 264; 2015), the image was incorrect and did not depict a hydrogen balloon. The sentence referring to the image should have read 'Molecular H₂ filled one of the first balloons used to carry people in 1783 (pictured), and the fuel tanks of rockets two centuries later, permitting the inquisitive to explore further and further.' These errors have been corrected in the online versions after print: 18 March 2015.