

FROM SIR WILLIAM GROVE TO TODAY: FUEL CELLS AND THE FUTURE

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Introduction

The history of the fuel cell dates from Sir William Grove's invention of the gaseous voltaic cell, which he first described in 1839. Grove was the quintessential nineteenth century amateur scientist, who nonetheless made a number of important discoveries. In later editions of his book [1], he describes fuel cells operating on many different reactants, including ethylene and carbon monoxide, as well as hydrogen. He should also be remembered for being perhaps the first person to appreciate the law of the conservation of energy [2], anticipating Helmholtz by one year. His scientific discoveries are all the more remarkable for the fact that his public recognition was as a jurist.

Grove published a description of the working of the first fuel cell in February 1839 [3]. This included the mechanism of a single cell, consisting of hydrogen and oxygen in contact with two platinized platinum electrodes. In that paper, he alluded to the possibility of combining several of these in series to form a gaseous voltaic battery, which he described for the first time in 1842 [4]. This description was followed by other papers [5].

The battery consisted of fifty single cells, each with anodic and cathodic platinized platinum foils one quarter of an inch wide. The most important observation that Grove made was his famous statement concerning the necessity for a 'notable surface of action' between the gas, electrolyte and electrode phases in his cells. His language makes many of the points that have been reiterated, in somewhat different form, during the age of the modern fuel cell, since about 1955.

Grove's words in his 1842 paper are worth quoting again:

"As the chemical or catalytic action . . . could only be supposed to take place, with ordinary platina foil, at the line or water-mark where the liquid, gas and platina met, the chief difficulty was to obtain anything like a notable surface of action. I determined to try the platina platinized . . . It is obvious that, by allowing the platina to touch the liquid the latter would spread over its surface by capillary action and expose an extended superficies to the gaseous atmosphere."

The expressions in italics, taken together, constitute the leitmotif of the development of today's fuel cell electrodes.

As he stated himself, Grove's series of fuel cells were hardly practical devices for power production from hydrogen and oxygen, indeed, they were scarcely more than capable of parlor demonstrations. Their capabilities for delivering current were strictly limited by the small effective active area of each electrode, which was probably little more than 10 mm^2 , representing a single meniscus about 2 mm high on a piece of platinized platinum sheet 6 mm wide. However, as the above quotation shows, he did realize the need for the highest area of contact between the electrolyte, the gaseous reagent and the electrocatalytic conductor, *i.e.*, the 'notable surface of action'. Trying to acquire this optimized reaction surface has remained the basis of fuel cell research and development ever since. Because of this realization, Grove can be truly said to be the inventor of the fuel cell.

The first modern fuel cell structure: Mond and Langer

Following Grove, the concept of increasing the 'surface of action' as a means of increasing performance was taken up by Mond and Langer [6], whose June 1889 paper gives a list of some fifteen papers published since Grove's first experiments, including one by Lord Rayleigh [7]. However, they state that up to that time the subject has been given 'very little attention'.

Mond and Langer were the first workers to try to improve upon Grove's electrodes by giving them a three-dimensional form. Grove's electrodes had a two-dimensional meniscus in which current was collected parallel to their plane. Mond and Langer made the electrode structure porous, and rotated it by 90° , thus creating a structure with all the features of the modern fuel cell. Each consisted of a diaphragm, made of a porous non-conducting substance (plaster of Paris, earthenware, asbestos, pasteboard), with electrodes consisting of perforated platinum or gold leaf as a current collector, contacting active surfaces of platinum black. The diaphragms contacted the gases on each side, and could be placed 'side by side or one above the other'. Their cells operated on hydrogen and oxygen at 0.73 V and a current density of 3.5 mA/cm^2 . In contrast, the phosphoric acid fuel cell of today operates at the same voltage, but at a current density 60 times higher, and more advanced systems can increase this current density by a further factor of ten. Apart from using newer materials, these cells are fundamentally similar to the Mond and Langer design, and they use a thin diaphragm carrying the electrolyte to reduce internal electrical resistance, always a major irreversible loss at high current density.

The major technological change in modern cells is a microengineered control over the meniscus, which in the Mond and Langer cell would have flooded the electrode structure, thus reducing the internal volume open to the gaseous reagent, the area available for reaction, and thus the current density. For this reason, Mond and Langer's cells showed a voltage that

decreased by about 10% per hour as a function of time, as product water collected in the acid electrolyte at the oxygen cathode. In modern cells, a great increase in the 'surface of action' with prevention of flooding is carried out by two approaches: the use of graded porosities, so that suitable micro-interfaces are maintained by capillary action, or by the use of a non-wettable additive, which locally creates zones empty of electrolyte, serving as gas microchannels within the electrode structure. These are discussed later.

A further advance was Mond and Langer's realization of the great efficiency of the electrochemical process compared with that of the thermodynamic engine. "We prefer to work ... with an e.m.f. of about 0.73 V ..., which gives a useful effect of nearly 50% of the total energy contained in the hydrogen absorbed in the battery." They also showed that water gas containing 30 - 40% hydrogen, produced by the gasification of coal would operate the fuel cell, at least for short times.

In summary, Mond and Langer's concept contained all the elements of the modern low-temperature fuel cell, except a means for maintaining an optimized three-dimensional 'notable surface of action' within the electrode film, instead of the less efficient two-dimensional structure used by Grove. Though it may not have been widely noticed, the year of this Symposium is therefore also the centennial of the first modern fuel cell concept.

The age of coal

Mond and Langer had realized that coal could be used as a source of hydrogen for the fuel cell, whereas Grove stressed only the use of pure hydrogen derived, for example, from zinc dissolution. While coal would have been used to produce the zinc, the overall concept would have had an energy efficiency too low to be of practical value. In work following that of Mond and Langer, emphasis shifted from hydrogen to more common and practical fuels such as coal, reflecting Ostwald's visionary hope of 1894 that the 20th Century would become the Age of Electrochemical Combustion, with the replacement of the steam Rankine cycle heat engine by much more efficient, pollution-free, fuel cells. In his well-known paper [8], Ostwald stressed the wastefulness of the steam-engine, with its then heat-to-work efficiency of 10%. He stated that the new way must be founded on electrochemistry, which could allow the theoretical amount of work to be obtained from coal, acid electrolyte and air, so that fire would not be the only method of effecting change, but would in future be replaced by electricity. One aspect, familiar to modern ears, that he stressed would be the lack of pollution: 'kein Rauch, kein Russ', no smoke, no soot. The dream of the late nineteenth century remains the dream of the late twentieth.

Ostwald's vision did not happen, for reasons that were largely connected with the slow electrochemical reaction rates of common fossil fuels, but which also resulted from the advent of the various types of internal com-

bustion engine using cleaner liquid (or gaseous) fuels. Competition from the latter resulted in the demise of the electric storage battery for transportation applications, and led to a lack of interest in electrochemical power in general, and in the development of the fuel cell in particular. We can also suppose that this Utopian view of the world, as seen from the perspective of the nineteenth century, might have become closer to reality had it not been for the wars of the twentieth, and the attendant cynicism and lack of care for human progress that they have characterized.

The outstanding researchers of the 'Age of Coal' were Jacques [9] and Baur [10]. Jacques, working about 1895, seems to have been the first to make large systems, including a 1.5 kW battery with about 100 small tubular cells, and later, a battery with a design power of about 30 kW. The cells consisted of cylindrical iron pots as cathodes, supplied with air via distribution tubes, with internal coke rods (3 in the case of the 1 kW-scale cells) as cathodes. Unlike Mond and Langer, with their modern concept of the immobilized electrolyte for mechanical control, Jacques used free electrolyte cells with molten KOH at about 450 °C. High performance (reputedly 100 mA/cm², 1.0 V) was obtained, so that the large cells (about 1.2 m high, 0.3 m diameter) were capable of over 300 W each. Such coke-air cells were suggested for all-electric naval vessels, as well as for urban power: 'think of a smokeless London', is a quotation from his article.

Jacques' claims were investigated by Haber and Brunner [11] in 1904, who showed that the anode operated via redox systems (manganite-manganate) giving favorable kinetics. They showed that Jacques' electrolyte was not invariant, since carbonate formation resulted as the carbon anode reacted. Today we realize why the iron cathode in the molten caustic electrolyte does not require a 'notable surface of action'. It is also a redox system involving molecular oxygen chemically dissolved as peroxide, so long as the electrolyte remains as hydroxide. After the rapid neutralization of the electrolyte, reaction stops. The spent electrolyte must be replaced or regenerated, in practice probably requiring more energy than the cell produces. Jacques thought that the nitrogen in the air bubbling through the melt would be sufficient to remove the excess carbonate as carbon dioxide, but unfortunately this is not so. While he acknowledged that his cell was not suitable for use with coal, because of its lack of adequate conductivity and to the large amount of ash produced (he did not mention sulfur), it was clear that KOH was not a practical electrolyte for use with carbon. The cell was essentially a large primary battery, unsuitable for continuous use.

Baur and Ehrenberg [10] attempted to use coal directly, again using carbon as a model, but this time with invariant electrolytes, such as molten carbonates. After this time, interest fell in the direct use of carbon (coal) as a fuel. The problems remained the same: the formation of ash, the poor conductivity, and the need for some method of continuously feeding the solid fuel. Muscle-power was of course economically adequate for this in the nineteenth century.

Improvements

As can be seen from the above, fuel cell developments from Grove's time to the first half of this century resulted in a series of dead-ends. Progress, or rather lack of it, revolved around the use of unsuitable chemistry and faulty engineering. While it is easy to speculate, with hindsight, on what might have been, the elements to make practical devices were there. Baur, *et al.* [12], working in 1922, used molten carbonate electrolyte with gas-operated anodes. In many respects, their cell structure was a high-temperature version of that of Mond and Langer, though with tubular, rather than planar, geometry. For the first time, they consciously used the concept for maintaining the 'notable surface of action' of the electrodes, already implicit in Mond and Langer's work, by the use of capillarity. The electrolyte of the cell was contained in a matrix powder material corresponding to Mond and Langer's diaphragm. If this is in contact with an electrode in porous form, whose range of pore diameter overlaps that of the matrix, capillarity will determine that if the latter is filled with electrolyte that wets all the components, then fine pores in the electrode will be filled with electrolyte, whereas coarse pores will remain empty. Thus, the latter will be filled with gas, and the resulting convoluted structure will supply the required 'surface of action'.

Starting in 1933 with the earliest work of Bacon in England (reviewed in ref. 13), the fuel cell can be said to have reached adolescence. Bacon wished to use ordinary materials, *i.e.*, no noble metals, a non-corrosive environment for maximum lifetime, and the highest possible electrode reaction rates (measured in current density, A/cm²) at the highest practical cell voltage, *i.e.*, efficiency. Reaction rates increase at high temperatures and pressures, *i.e.*, therefore Bacon, associated with Parsons' turbines, marine engineering and high-pressure boilers, used the engineer's approach. His fuel cell was essentially in a high-pressure boiler. While he would have preferred to use steel, nickel was the best compromise. It and its oxide are stable in alkaline solution at both the hydrogen and oxygen electrode, respectively, though it is not stable in acid. Hence, the electrolyte was hot potassium hydroxide solution, circulated to remove heat from the high-power system, and to remove water. To maintain an invariant electrolyte composition, a carbonaceous fuel, or air containing carbon dioxide, was excluded. Hydrogen was therefore the fuel, as in Grove's cells, so that with pure oxygen as the complementary oxidant the product was pure water. Bacon conceived his system as a storage unit, in which hydrogen and oxygen could be produced with off-peak electrical power, and consumed when required. He thus had in mind Grove's "effecting the decomposition of water by means of its decomposition... (which) exhibits such a beautiful example of the correlation of natural forces".

Circulation meant a free electrolyte, hence Bacon used an electrode structure that combined the porous properties of Mond and Langer's and Baur, Treadwell and Trumpler's matrix and electrodes: a wetted, fine pore

structure facing the electrolyte, and a more open structure on the gas side. In this respect, he followed the earlier work of Schmid [14], who developed the first 'Diffusionsgaselektrode' in 1923 for use in aqueous acid electrolytes. This had a dual-porosity structure with a coarse-pore graphite gas-side layer and a fine-pore platinum electrolyte layer.

Bacon's cell thus combined this with a distillation of the work of previous researchers: pure hydrogen and oxygen from Grove, the parallel structure of Mond and Langer, the electrolyte of Jacques without the error of carbonatation, and a compromise in temperature and composition between the purely aqueous and molten electrolyte systems.

For a long cell lifetime, the temperature of the Bacon cell was limited to 200 °C, which meant that a pressure of 45 atm was possible to achieve high performance. Bacon thus obtained about 1 A/cm² at 0.8 V, or 0.4 A at 0.85 V, which would be considered remarkable even today. Parallel with Bacon's later work was that of Justi and Winsel in Germany [15] which achieved a similar performance at lower pressures and temperatures by increasing the nickel electrode internal area, *i.e.*, the 'notable surface of action'. This they did by means of the high-surface area Raney nickel DSK (Doppelskelett Katalysator) electrode, whereas Bacon used electrodes made from sintered carbonyl nickel powders. This reflects the fact that electrode structures give us a choice: high temperature increases activity, but causes loss of surface area by sintering and compaction, therefore all structures and operating conditions are compromises.

Bacon continued to develop his cell up to the early 1960s, as long as funding was available in England. After this, the concept was transferred to the Pratt and Whitney Division of United Aircraft Corporation (now United Technologies Corporation) in Connecticut, where it was modified for space use. This required reduction of the pressure vessel weight by reducing the pressure by a factor of ten, which required a simultaneous increase in temperature to 260 °C and an increase in electrolyte concentration to 75% KOH to prevent boiling. Similarly, the circulating electrolyte was eliminated, and heat and water were removed by a closed-loop hydrogen cycle. The increased temperature did not compensate for the lowered pressure from the performance viewpoint, but the system was still capable of 0.15 A/cm² at 0.85 V [16].

Bacon's cell, as modified by Pratt and Whitney, was the on-board power system for the Apollo lunar missions. Without this technology, the only one available at the time with sufficient power and energy densities, the lunar landings would have been impossible.

The non-wetting electrode

Above, we alluded to another method by which Grove's 'notable surface of action' could be achieved: the notion of 'controlled wetting'. While this is almost inconceivable in a molten electrolyte, in aqueous solutions it is

possible because of the lyophobic and lyophilic properties of many materials. By the early 1930s, the need for a new concept to open up the electrode porosity was realized. One method, that of Tobler [17] in 1933, made the electrode into a thick stationary bed with much open porosity. This was not satisfactory, because it separated the active parts of the electrodes by too great a distance, and thus introduced a large internal resistance. Mond and Langer's 'closest approach' concept for the anode and cathode could thus not be used. Wetproofing electrodes (with highly unsuitable paraffin wax) was perhaps first used by Heise and Schumacher in 1932 [18].

After about 1950 Teflon (ptfe) became available. It was first used in platinum electrodes for acid electrolyte, and carbon electrodes for alkaline electrolyte, before 1964 - 1965 at General Electric and Union Carbide respectively [19, 20]. The use of this remarkable material made the aqueous (liquid) electrolyte fuel cell in its modern form possible.

New developments of the 1960s

In the early 1960s, attention turned again to the platinum-catalyzed acid electrolyte cell in two different forms. One used a polymer acid electrolyte, which made it simple and reliable. Its combined electrode-electrolyte structure made it automatically water-rejecting, and at its original modest power levels (37 mA/cm^2), it required no wetproofing. Its original electrolyte material restricted its operating temperature and thus its performance, but it was developed by General Electric for the modest power requirements (1 kW in a 29 kg unit) of the Gemini missions, where its ability to produce potable water for the astronauts was a great advantage in the lightweight capsule. Its test vehicle, a small General Electric fuel cell, became the first to go into space in a suborbital flight on October 30, 1960.

The second acid technology was developed to attempt to use carbonaceous fuels directly, which is impossible in cells with alkaline electrolyte. The chosen electrolyte made use of the great stability of phosphoric acid to obtain the highest operating temperature possible (150 - 200 °C) for the greatest reaction rates. The breakthrough was the use of stable ptfe as a wet-proofing agent in the high-area platinum black electrodes. These allowed the whole inside area of the electrode to become a convoluted meniscus, increasing the 'surface of action' to close to its physical limits. However, carbonaceous fuels still showed disappointingly low rates in this fuel cell environment, even with excessive amounts of noble metal catalysts at the anode. These low rates were due to electrocatalytic poisoning effects. The above work is reviewed in ref. 21. As other speakers at this Symposium describe, the phosphoric acid fuel cell is now favored for utility use (stationary power generation), where its waste heat at almost 200 °C is a valuable source of energy for raising steam to produce hydrogen mixtures by reforming of natural gas.

In parallel, work started in the Netherlands under Broers and Ketelaar on molten salt fuel cells using molten carbonate electrolyte at 650 °C [22].

These followed earlier work of Greger [23] and Gorin [24], which were in turn based on that of Baur *et al.* [12]. The molten carbonate cells could use nickel-based electrodes made from sintered powder similar to Bacon's. A mixed alkali metal carbonate was the only molten salt allowing low-polarization electrode reactions with carbonaceous fuels. Finally, Weissbart and Ruka [25] raised the operating temperature further, to 1000 °C, and adapted the doped zirconia conducting ceramic oxide of the 'Nernst Glower' of 1900 [26] as a solid electrolyte.

From the beginning, it was noted that laboratory high-temperature cells would not operate directly on hydrocarbons, which showed cracking and, as in the medium-temperature phosphoric acid cell, disappointing reaction rates. It was finally shown that reformat (the gas resulting from steam-reforming of the hydrocarbons) was an effective fuel, which could be used directly in the high-temperature cells, and after water-gas shifting to prevent poisoning by carbon monoxide in the phosphoric acid system. Thus, hydrogen (in the form of mixtures) had again become the fuel of choice. By the late 1960s, these developments had laid the groundwork for the fuel cell developments of the last twenty years.

Today and the future

The fuel cells developed since 1970 have been characterized by the elimination of diffusion limitations in electrode structures by better understanding of the nature of Grove's 'surface of action', by the reduction of costly catalyst loadings in the phosphoric acid system by a factor of about 200, still accompanied by an increase in performance, and finally, improvements in lifetime, making practical operation over five years or more possible. One disappointment has been the lack of breakthroughs in increasing the specific rates of the oxygen electrode process in low- and medium-temperature systems, though some progress has been made.

Above all, emphasis has been on engineering. When hydrocarbon feedstock (*e.g.*, methane) is used as fuel, the chemical plant converting it to impure hydrogen must be integrated with the fuel cell to ensure maximum efficiency. Now, promised efficiencies based on the higher heating value of methane at practical electrode reaction rates have been raised to about 45% in phosphoric acid systems and to 50% and 60% in the solid oxide and molten carbonate systems respectively. These high efficiency values, combined with very low atmospheric emissions of fuel cell systems and the possibility of dispersed, modular units, may soon revolutionize power generation, one century after Ostwald's prediction. They may come in time to have some impact on the 'greenhouse effect', and tropospheric pollution in general.

Specific power outputs of fuel cell generators have increased dramatically in twenty years, in the case of the pure hydrogen-alkaline aerospace system by two orders of magnitude. If pure hydrogen is used as the fuel, the large chemical engineering plant associated with the use of carbonaceous

fuels can be eliminated, allowing the use of lightweight non-polluting fuel cells with 50 - 60% thermal efficiencies in transportation. In the future, pure hydrogen may therefore be the fuel of choice, as Grove envisaged.

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