REVIEW

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On the history of solid electrolyte fuel cells

Abstract The path to the discovery of galvanic solid electrolyte gas cells (J.-M. Gaugain 1853) and to the first industrially produced solid electrolyte gas cells (Nernst lamps 1897) is described. The development of the fundamentals of solid electrolyte fuel cells started with the work of Haber 1905, Schottky 1935, Baur 1937 and Wagner 1943. Extensive work in the field of solid oxide fuel cells (SOFCs) was done in the fifties by Peters and Möbius. After 1960, a rapidly growing number of scientists worked on the different problems of SOFCs, and by 1970 the basis was established on which the broad technologically orientated development of SO-FCs proceeds today.

Key words Solid oxide fuel cells · Solid electrolytes History · Nernst lamp · Galvanic gas cells

The path to the first industrially produced solid electrolyte gas cells

Starting in 1800, Davy carried out many investigations into the electrolysis of water and aqueous solutions. Experiments using more and more concentrated solutions of alkali hydroxides led to melting flux electrolysis and in 1807 to the discovery of alkali metals [1]. Davy observed that dried solid alkali compounds were non-conductors but became electrically conducting through just a little moisture. For Faraday it seemed to be an important law that many substances, electrically conducting in the liquid state, lost their conductivity during solidification [2]. In his continuing investigations, Faraday introduced the basic terminology of electro-chemistry, and with the aid of many results concerning the concept "electrolyte" in 1834 he came to the clas-

sification of substances into first and second types of conductors [3]. This meant an essential simplification, for example compared with the distinction between five classes by Erman [4]. But it is interesting that in this classification, given in 1806, even the term "unipolar conductor" plays an essential role; Erman observed that when "solid alkali soaps were brought into the highest degree of dryness" effects were only obtained at one terminal of the applied current source.

Faraday encountered problems with the classification of silver sulfide, which exhibited conductivities comparable to metals in the high temperature range, but, in contrast to metals, lost its conductivity upon cooling down [2]. Hittorf (1851) devoted himself to this special problem and proved that Ag_2S is electrolytically decomposable [5]. The generation of a counter voltage (polarisation by chemical precipitation) during the passage of a current was recognised as a characteristic feature of electrolytic conductivity of solids [5, 6], and this led to the discovery of an increasing number of solid conductors of the second class.

As early as 1774 Cavendish [7] had observed an increase in the conductivity of glass on heating. The electrolytic nature of this conduction was discovered by Beetz [8] and Buff [9] in 1854. Using mercury, zinc amalgam, various solid metals, carbon, and pyrolusite (MnO_2) as electrodes, Buff demonstrated galvanic cells and batteries free of water "in which glass takes over the role of the moist conductor", and he investigated the associated voltage and polarisability.

A short period before, Gaugain [10] and Becquerel [11] had published experiments on the thermoelectricity between metal contacts on glass and porcelain. Buff [9] reproduced the results, which turned out very differently depending on the position of the contacts in oxidising or reducing regions of flames, and he interpreted the voltages as a mixture of thermoelectric forces and voltages which he had previously observed between bare platinum wires in flames [12]. But Gaugain investigated his cells, which at first were made of two tubes of glass, platinum wires, air and alcohol vapour, in more

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detail [13]. He observed their effect on capacitors and their delivery of current, the polarity of the electrodes and their behaviour if the electrode metals or the gas supply were changed. He also noted the large voltage alteration when different gases were mixed with oxygen beyond a certain proportion (known today as the jump at the stoichiometric point $\lambda = 1$), and phenomena associated with an *iron/air* cell which convinced him of the decisive role of oxygen in the electrode reaction. Although restricted by the lack of sensitivity of the available measuring device (a leaf electroscope) so that small voltage differences could not be detected, Gaugain nevertheless found that "the new source of electricity possesses all the characteristic features of an aqueous-electric cell", and thus *he discovered in* 1853 *galvanic solid electrolyte gas cells*. (See the translation at the end of this paper.)

A glass was also the first solid where the law of Faraday was verified by transference measurements. Warburg observed [14] that during electrolysis between sodium amalgam (anode) and mercury (cathode) at 300°C, a soda-lime glass remained transparent, but with other electrodes, interfacial layers exhibiting large electric resistances were produced. Obviously only sodium ions migrated through the glass, which could therefore be classified as one of the unipolar conductors mentioned by Ohm [15].

Towards the end of the 19th century the term "solid electrolyte" was in use, and many facts were known about the behaviour of these materials. The "Science of Electricity" by Wiedemann (1893/98) includes the chapters "Conductivity of Solid Salts" and "Determination of the Electromotive Force. - Two Metals and Solid Electrolytes" and "Electrolysis of Solid Electrolytes" [16]. However, in Ostwald's "Treatise on Electrochemistry" (1885/1917) solid electrolytes are not mentioned [17]; they were at that time a domain of the physicist.

A technological interest in solid ion conductors first arose in connection with the development of electric lighting devices. Early carbon filament lamps manufactured since about 1880 could not compete with the existing gas incandescent light. In 1897, Nernst suggested in a patent [18] that second-class conductors in the form of a thin rod could be made electrically conducting by means of an auxiliary heating appliance and then kept glowing by the passage of an electric current. At first Nernst mentioned only "lime, magnesia, and those sort of substances" as appropriate conductors. Later investigations stimulated by experiences with gas mantles led to his observation "that the conductivity of pure oxides rises very slowly with temperature and remains relatively low, whereas mixtures possess an enormously much greater conductivity, a result in complete agreement with the known behaviour of liquid electrolytes" [19]. He pointed out that, for example, the conductivity of pure water and pure common salt is low but that of an aqueous salt solution is high. In a short time many of the mixed oxides which exhibit high conductivity at elevated temperatures [20], including the particularly favourable composition 85% zirconia and 15% yttria [21], the so-called Nernst mass [22, 23], were identified. The thesis studies of Reynolds 21 inspired by Nernst, and presented in 1902, were a considerable achievement. These concerned the conductivity in the range 800–1400°C of numerous binary and ternary systems, among others, formed by ZrO_2 with the oxides of the elements La, Ce, Nd, Sm, Ho, Er, Yb, Y, Sc, Mg, Ca, Th and U, including investigations on the role of composition, concentration, direction of temperature alteration (hysteresis) and other phenomena.

Figure 1 shows one of the many designs of the Nernst lamp [25, 26]. When the lamp is switched on, the voltage is applied to the Nernst rod, h, and to the parallel heating resistor, i. Both these components were incorporated in a glass envelope containing air. After sufficient preheating, the current starts flowing through the Nernst rod h and through the winding k of an electromagnet b. At a specified electric current the magnet switches off the heater by opening the contacts between m and l and then the Nernst rod emits light due to resistive heat generation.

The light efficiency of the Nernst lamp exceeded that of the carbon filament lamp by nearly 80%. However there were problems. It was difficult to fabricate reliable contacts to the glower, and the platinum leads and heater made the lamp expensive. The glowers had to be prevented from melting with the aid of special series resistors. It was necessary to wait in darkness for half a minute after switching on the lamp until the light appeared. In view of these and other disadvantages, interest in the Nernst lamp, although considerable for a few years, soon disappeared in 1905 with the introduction of the first tungsten filament lamps, which were much simpler and permitted a substantial increase in the light efficiency by raising the glow temperature.

The Nernst glowers were similar to metallic conductors in that decomposition did not occur with the passage of direct current. Nevertheless, Nernst was
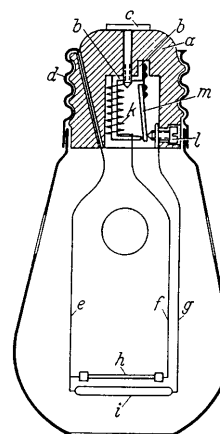

Fig. 1 Arrangement of a Nernst glower in a lamp (DRP 114 241, filed Apr 9,1899)

convinced that his glowers were ionic conductors, and he assumed that in zirconia the oxidic additions were dissociated to some extent and able to provide the necessary charge carriers [19]. He observed evidence of oxygen transport, but believed that metal cations were also deposited by the direct current, and, after immediate oxidation by the surrounding air, the resulting oxides diffused back into the glower. Transference number measurements were not performed on the Nernst mass at that time. It was not until 1943 that Wagner ([27] in memoriam Walther Nernst, 18 November 1941) recognised the existence of vacancies in the anion sublattice of mixed oxide solid solutions and thus explained the conduction mechanism of the Nernst glowers. We now know that Nernst glowers are oxide ion conductors and the platinum contacts behaved as air electrodes. It follows that *Nernst lamps were the first commercially produced solid electrolyte gas cells.*

The development of fundamentals of solid electrolyte fuel cells up to 1960

Electrochemistry was given an important impetus by its connection with thermodynamics, discovered by Helmholtz in 1882 [28]. In 1894 Ostwald illustrated the advantages resulting when energy from coal is produced not with a steam engine but directly with a galvanic cell [29].

The agreement between the voltages measured with galvanic solid electrolyte gas cells and calculated thermodynamically had already been verified by Haber and coworkers in 1905. From 330 to 570°C they used glass and from 800 to 1100°C porcelain as the electrolyte, and partly platinum, partly gold as the material for the electrodes in cells, first with C, CO, CO_2 and O_2 [30], then in oxyhydrogen cells, and then in hydrogen and oxygen concentration cells [31, 32]. Typical phenomena such as the dependence of the voltage on the gas flux, deviations from zero ('asymmetry voltages'), and with decreasing temperature increasing sluggishness in the establishment of constant voltages were observed. Parallel to the publication of the results, Haber filed the first patent on fuel cells with a solid electrolyte [33] (Fig. 2). To compensate for alterations in the solid
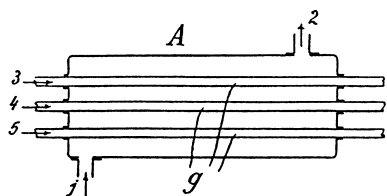
Fig. 2 First diagram (1905) of a fuel cell with solid electrolytes [33]. Generator gas passed from *1* to *2* through chamber *A* (440°C) with parallel glass tubes *g* covered on both sides with thin layers of noble metal and swept inside by air

electrolyte of glass by the migration of ions caused by current, he proposed to exchange the gases in the electrode chambers as soon as disturbing alterations were noticed.

The decomposition equilibria of metal oxides were investigated in 1916 by Treadwell in the region of 1000°C, with quartz and porcelain as solid electrolytes and with a silver electrode, oxygen-saturated at normal pressure, as the reference system [34]. After these investigations Baur and Treadwell filed a patent on fuel cells with metal oxides as the electrodes and ceramic solids with salt melts in the pores as electrolyte [35]. Only after many fruitless experiments with liquid electrolytes of different types did Baur 1937 come to the conclusion that fuel cells have to be made completely dry [36]. But the extensive empirical search by Baur [22, 37–39] and other authors up to the 1950s for suitable solid electrolytes, covering glasses, porcelains, clays and a great variety of oxide mixtures, were unsuccessful.

The empirical phase of the development of solid electrolyte fuel cells was overcome only after many general advances in research on solids. These included development of X-ray structure analysis, new knowledge on the ion conduction of solids from the measurements of transport numbers by Tubandt (first detection of unipolar conduction by anions), the establishment of the theory of disorders in solids connected firstly with the names Frenkel, Schottky, Wagner and Jost, and the development of the methods for the investigation of diffusion processes in solids with stable and unstable isotopes.

Starting from knowledge of effects caused by small excesses of components in salts and oxides, Schottky investigated problems of fuel cells with solid electrolytes in 1935 [40] and suggested that a comprehensive patent should be applied for by Siemens and Halske [41] (Fig. 3). He pointed out the advantages of solid over liquid electrolytes such as the feasibility of small layer thicknesses, less disturbance by ambipolar and neutral diffusion processes, and small absolute concentrations for the realisation of chemical potential differences in solids. He considered, among other things, porous metallic electrodes and electronic semiconductors forming intermediate or main electrodes (with the demand that no continuous series of mixed crystals with the electrolyte material should be formed), and he discussed cyclic processes for the continuous supply of the electrode chambers, self-regulation of the temperature, and repeated temporary chemical alternation of the polarity of the cells by changing the gas supply. Concerning the electrolytes, for which Schottky demanded a conductivity near 0.3 S/cm, halogenides, sulfates, carbonates and phosphates but no oxides were taken into consideration. An electrochemical exploitation of the combustion of coal seemed to be less feasible than that of the formation of hydrogen chloride.
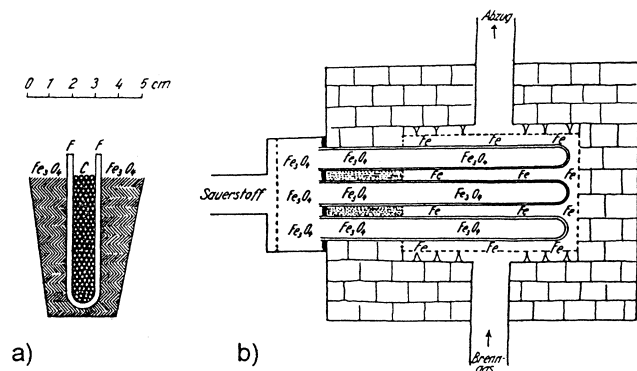
Zirconia ceramics was first used in fuel cells in 1937 by Baur and Preis [22]. They wrote on the Degussa tube crucibles used (16 mm × 12 mm × 190 mm): "Unsur-
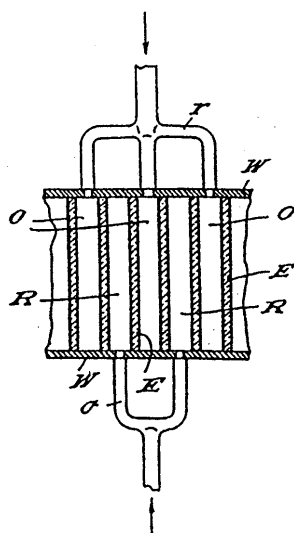
Fig. 3 Solid electrolyte fuel cell specified in a patent by Siemens and Halske [41] (inventor Schottky W, filed Apr 6, 1935). *W* walls of a closed electrically isolating casing, *E* solid electrolyte disks with a thickness of the order of mm, *O* chambers with O_2 or air, *R* chambers with gas mixtures containing CO and CO_2, *o* and *r* gas lines to the chambers O and R

passed is the Nernst mass. But even this mixture is not satisfactory because the current enhances resistance considerably ... by electrolytic shift (migration away of the cations)". The problems were possibly caused by the material used for the cathodes (mill scale, Fe_3O_4, Fig. 4), which at 1000°C in air it is to be expected (in accordance with results obtained at the same place, Zürich [34]) to oxidise to form poorly conducting Fe_2O_3 (considered by Biefeld in 1944 [42]). So the wrong conclusion was drawn: "One has to look for an improvement of the Nernst mass or to put alongside it solid conductors of higher value."
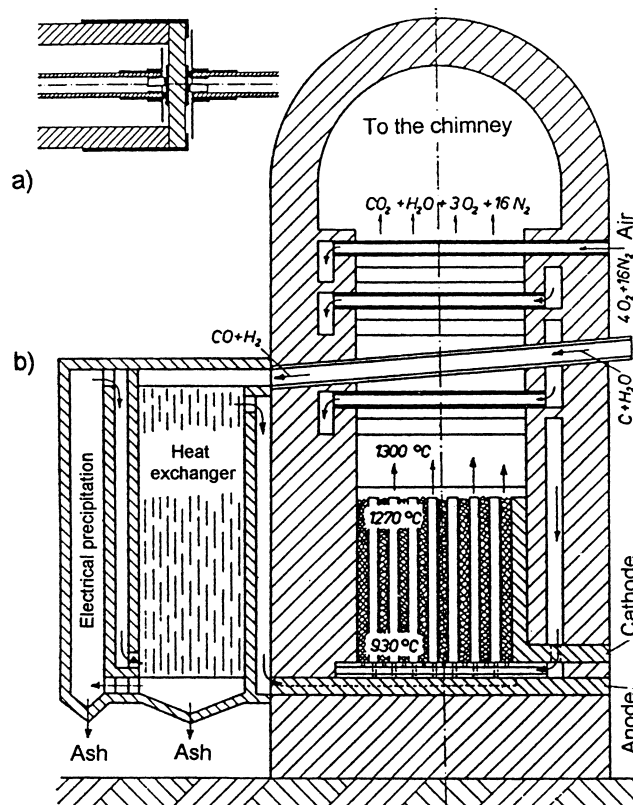
After his statements on the mechanism of conduction in the Nernst glower, Wagner had pointed out that, for fuel cells with solid electrolytes, solely anion conductors could be taken into consideration, and for this

reason systematic investigations of the mixed crystal systems of the type of the Nernst glower mass are desirable [27]. In 1951 Hund confirmed, with X-ray crystallographic and pycnometric investigations, the existence of oxide ion vacancies in the Nernst mass [43]. Hauffe, having worked from 1936 to 1940 in Darmstadt with Wagner [44], followed up the suggestions received and left to Peters (in 1951 in Greifswald) the investigation of the lattice structure and the electric conductivity of some mixed oxides of the type of the Nernst mass (ZrO_2-Y_2O_3, ThO_2 and CeO_2 with Y_2O_3 and La_2O_3). After Hauffe had left for Berlin, the thesis was finished in Rostock in 1953 [45]. There in 1954 Peters gave Möbius the task of pursuing the subject with the preparation and investigation of galvanic cells using the mixed-oxidic phases covered in his thesis.

The investigations [46], using model fuel cells (Fig. 5a), were to lead to the most appropriate mixed oxides and electrode arrangements, the requirements for the single component parts and the most favourable conditions of working. After experiments with iron oxides, magnesium ferrite (following Biefeld [42]) and composites of iron and alumina, the electrodes were prepared mainly with thin porous layers of platinum, nickel and iron to facilitate the solution of many complex problems. Very soon it was seen that completely

Fig. 4a, b Fuel cell arrangement of Baur and Preis (1937) [22, 35–39]. **a** Investigated cells also with Nernst mass as solid electrolyte (*F*). **b** Proposal for the realisation of batteries of such fuel cells

Fig. 5 a Cross section of galvanic cells with oxides as solid electrolyte investigated by Peters and Möbius (1958) [46, 48]. **b** Draft of an SOFC plant as a basis for calculations in reflections on [46]; see [79]

gastight solid electrolyte discs of highly pure substances had to be produced if the measurements were to lead to useful results. Compounds of thorium, cerium and lanthanum were effectively purified as ammonium double nitrates by crystallization from hot concentrated nitric acid and by fractional precipitation of hydroxides (La). Bearing in mind experience of oxide ceramics [47], powders of mixed oxides and pressed solids were produced with the purified substances and various gastight discs, 25 mm in diameter and 1–2 mm thick, could be sintered at temperatures up to 1920°C in a stream of oxygen on an underlay stack Al_2O_3 $MgAl_2O_4$ ThO_2 in alumina protecting tubes in a Tammann carbon tube furnace (original Göttingen 1925). ZrO_2 for this investigation was available here at that time only in the form of a mixture with Y_2O_3 as a residue from the investigations of Peters (an embargo and the development of atomic industry made it difficult to obtain). In long investigations (in all, the preparation of 74 solid electrolyte discs and the carrying out of 100 experiments from 5 August 1955 to 3 July 1957 were recorded), measurements were made of voltages of cells with various compositions of solid electrolyte, electrodes and gas phases in the temperature range between 300 and 1350°C, and results were compared with thermodynamically calculated values.

A fundamental problem in achieving high efficiency of solid electrolyte fuel cells was seen to be the possibility of internal short circuit by electronic conduction of the electrolytes. Now the results of the measurements made clear that in the case of Th-La mixed oxides, even with only 1 mol% $LaO_{1.5}$ the ion transport number 1 was reached, admittedly only with reducing gas on both electrodes (in CO,CO_2 concentration cells); in the *oxygene/air* cell even at 10 mol% $LaO_{1.5}$ this number came only near 0.8. Solid electrolytes of $Ce_{0.9}La_{0.1}O_{1.95}$ broke into pieces in $CO,CO_2/O_2$ cells between 700 and 840°C, reaching the mean ionic transport number 0.8. For the available ZrO_2 solid electrolyte (with 50 mol% $YO_{1.5}$) in the *oxygen/air* cell, the ion transport number came above 0.93. With this solid electrolyte in a CO,CO_2, $Fe_3O_4/Pt,O_2$ cell, thermodynamical data were obtained from the cell voltage which were close to the data from the literature for the CO_2 dissociation equilibrium determined in other ways [48]. Corresponding data for the Boudouard equilibrium were obtained from the voltage of a $CO,C,Fe/Th_{0.9}La_{0.1}O_{1.95}/FeO,CO,CO_2$ cell using only the reactive carbon precipitated out of CO; the iron in metallic or oxidic form in the electrodes supported the establishment of the electrode potential catalytically.

The good agreement between measured and calculated data found in these cases was the basis on which the potentiometric determination of gas concentrations with solid electrolyte cells and first designs of probes for the in situ analysis of hot gases (reference electrode e. g. Ni,NiO or a gas with known oxygen partial pressure) were filed 1958 as an application for a patent [49]. Calculations of oxygen partial pressures in purified nitrogen using the measured cell voltages of solid electrolyte cells investigated were already performed by the end of 1955. [1] In accordance with the experience collected on fuel cells, potentiometric gas analysis with solid electrolyte cells was applicable to oxidizing and reducing gases. The fundamentals of gas potentiometry were presented accordingly [50], including the "neutral" transition field. Calculations and measurements in the case of potentiometric titrations of different gases were in good agreement over the whole range [51]. (The sudden change of the cell voltage of a *hydrogen/air* cell at the equivalence point when oxygen was fed to the hydrogen has already been shown graphically by Archer et al. [52, 53]). With this, the treatment of solid electrolyte fuel cells led to the phenomenon which today is used a millionfold in the lambda probes of cars. (A zirconia cell working potentiometrically was first proposed by LOOS in 1969 as a sensor for O_2 and CO for the regulation of the air/fuel ratio in cars, still without knowledge of the jump of the cell voltage at $\lambda = 1$ [54].)

On the basis of the results on ion transport numbers the investigations of Peters and Mann on metal, metal oxide systems, with $Th_{0.9}La_{0.1}O_{1.95}$ as the solid electrolyte, were performed not opposite O_2 but opposite CO,CO_2-mixtures [55]. Kiukkola and Wagner first used the advantageous CaO-stabilized ZrO_2 as the solid electrolyte for thermodynamical investigations [56], but they could not realise the intended measurements opposite a gas electrode because their solid electrolytes were porous (C. Wagner, Private communication to H. Peters).

The above-mentioned papers published in 1957/58 set off many activities in various parts of the world in the field of solid-state electrochemistry. In this development, solid electrolytes on the basis of ZrO_2 dominated immediately, for example in the first device described by Weissbart and Ruka for the measurement of oxygen with a high-temperature galvanic cell [57]. The intensive treatment of solid electrolytes on the basis of ThO_2 in Rostock had several reasons. In 1948, Ryschkewitsch [47] pointed out that a large-scale technical application of ThO_2 was still lacking, that in the 1950s in the development of nuclear energy it seemed that more zirconium than thorium was needed, and that mixed oxides with ThO_2 are crystallographically simpler than those with ZrO_2. The processing of the thorium compounds was done at that time without any measures for radiation protection.

The electronic part of conduction of electrolytes on the basis of ThO_2, increasing with the oxygen partial pressure (oxidation semiconduction), could be observed even with pure white mixed oxides (free from polyvalent cations). During the establishment of the electrode potentials there were signs of solubility of oxygen in the lattice. These facts led to the conclusion

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[1] This was an essential fact in a patent dispute between Babcock and Wilcox, Canada and Westinghouse Electric, USA, who claimed that the first measurements of oxygen with solid electrolytes were made in USA in May 1958.

that the electronic conduction observed arises in the anion sublattice and that generally in mixed oxides with oxide ion vacancies defect electrons can exist represented by monovalent negative oxide ions. The hole conduction even of solid electrolytes on the basis of ZrO_2 with practically 100% ionic conduction first made itself disadvantageously felt in cells with Ni,NiO reference electrodes for gas potentiometry [49, 58] when tested in air by the oxygen permeability, which was measured potentiometrically directly in 1965 [59]. The excess electron conduction after partial reduction of stabilized ZrO_2 (reduction semiconduction) arising in the cation sublattice was described by Schmalzried in 1962 [60].

Lack of clarity existed concerning the cause of relatively stable cell voltages repeatedly observed below 600°C with the *oxygen/air* cell, which sometimes far exceeded the expected thermodynamic values. The interpretation was given only 20 years later by Hartung, with the discovery that traces of combustible substances in the air or in the oxygen used determine the electrode potential in competition with the oxygen, increasing as temperature drops [61]. This effect is the basis of the development of hydrocarbon sensors today.

For the clarification of the properties of solid electrolyte ceramics with tungsten oxide and cerium dioxide, which Baur preferred to the Nernst mass [22, 37–39] and which were used repeatedly by other authors, the transport numbers of the electronic charge carriers in tungstates of Ce, Ca and Zn were determined in oxidising and reducing conditions and compared with those of $Zr_{0.85}Ca_{0.15}O_{1.85}$ [62]. The electronic transport through tungstates, depending strongly on temperature, as observed, excluded their application in fuel cells, because the electronic conductivity reduces the efficiency of fuel cells with decreasing current to zero, as has been shown theoretically [40, 46] but is often ignored.

For the understanding of the oxide ion conduction of the mixed oxides, there was the problem already seen by Wagner [27] that the radius of the oxide ions is larger than that of all cations in the crystals. As well as the concentration, it is always the mobility of the charge carriers which determines the conductivity of homogeneous bodies. By space-geometrical considerations it could be shown [46, 63] that the fluorite lattice in particular offers better possibilities for the motion of the larger anions than it does for the smaller cations; obviously a more favourable space structure does not exist. Furthermore, from geometrical calculations corresponding to the "excluded volume model" [64] it can be shown that with decreasing radius of the cations down to a lower limit the possibilities for the motion of cations grow more unfavourable and those of the anions grow more favourable. Several measurements of conductivities confirm the influence of cation size [65–68]. The result is also supported by the determination of the ion mobilities in Na_2S, which possesses antifluorite structure and reaches the highest known sodium ion conductivity [69].

That the cations are firmly held in their places in the oxide ion conductors has much importance for the long-term stability of fuel cells. The interpretation of the low cation mobility supported the suggestion of incorporating polyvalent cations in layers of mixed oxides with fluorite structure and producing stable electrodes at the oxide ion conductors by sintering [70] (aiming at a continuous series of mixed crystals with the electrolyte material, contrary to the demand of Schottky [41]). The layers of mixed conductors should ensure ideal conditions for the conduction of oxide ions and electrons and hence for transfer reactions in the electrodes. After these ideas had been represented in the Class of Chemistry of the Academy of Sciences in Berlin in 1958 [71] there were substantial doubts in the discussion; a statistical mixing of all the different cations in a homogeneous solid phase at high temperatures was considered to be very probable. These doubts induced investigations with radionuclides [72, 73] which confirmed the low mobility of the cations in mixed oxides with fluorite structure, in accordance with the results of Rhodes and Carter [74].

It turned out to be a misconception to think that even small concentrations of polyvalent cations in oxidic fluorite mixed phases produce a high electronic conductivity [75]. Layers with a high concentration of praseodymium at the cathode and a high concentration of cerium at the anode had to be realized in order to achieve anything near the conductivities aimed at [76]. Stable layers in both electrodes were obtained only with uranium as a cause of electronic conduction together with a good oxide ion conductivity. In the layers of mixed conductors, the course of the electrode reactions was to be extended from the three borderlines to over the whole area. This idea was confirmed by the result that thin mixed conducting interlayers between the pure electrolyte and the metallic conductor considerably reduced polarisation phenomena [77] and led to high current densities [78].

Following the investigations into model fuel cells, the possibilities for technical use in energy production from coal or fuel gases, for the electrolysis of water vapour and carbon dioxide, and for the separation of oxygen from air were considered in 1958 (H.-H. Möbius, unpublished paper "Zur Nutzanwendung von Festelektrolytelementen"—reflections on [46]). For the attainable performance density discussed already by Schottky [40] and Baur [22], the calculations for an electrochemical turnover of 95% demonstrated high gas flow rates and a temperature change of nearly 340 K between entering and leaving the aggregate of cells (Fig. 5b). After the experience with ceramic bodies, such requirements would obviously only be met with tubular cells. Even under favourable conditions only 60% efficiency was attained when the heat of the exhaust gases was used for the endothermic gasification of coal or for driving heat engines downstream of the fuel battery. In the plan for an aggregate of cells, series connection was not intended; current was to be taken

from tube cells 1 m long with contacting loose electronic conducting material poured into and between the cells. This conception, corresponding to that of Baur (Fig. 4), was to be turned down because the conductivity of available electronic conductors is much too low, and the resistance of the filling to high gas flow rates too high.

The early development of technically usable solid electrolyte fuel cells

Wagner initiated exhaustive investigations of solid oxide fuel cells with his paper of 1943 [27] in Germany and apparently with his paper of 1957 [56] in several other countries. After 1960, a rapidly increasing number of applications for patents were filed (only some of the early ones are mentioned here).

In the USA, during a short period in 1961/62, patents were taken out by four companies on solid electrolyte fuel cells, partly with series connection [80–86]. With knowledge of the oxide-ion conductivity of stabilized zirconia, the old ideas of carbon combustion in fuel cells [29, 30, 37] were also tested (Fig. 6).

The first publication in English on the new path, "A solid electrolyte fuel cell" by Weissbart and Ruka came out in 1962 [87]. At that time systems for energy supply in space ships were an important goal for which expense was no obstacle. From February 1962 to April 1963 in Westinghouse Electric, a team of 16 persons under the leadership of Archer developed solid electrolyte fuel batteries. Parallel flat-plate and tubular cells platinum electrodes were produced, optimized, and connected in series using a gold-nickel solder [52]. Flat solid electrolytes did not lead to great success; they resulted in bulky batteries and caused greater difficulties with sealing problems, in contrast to the tubular cells using a bell-and-spigot joint (Fig. 7). The main problem was the platinum anodes, which do not withstand prolonged
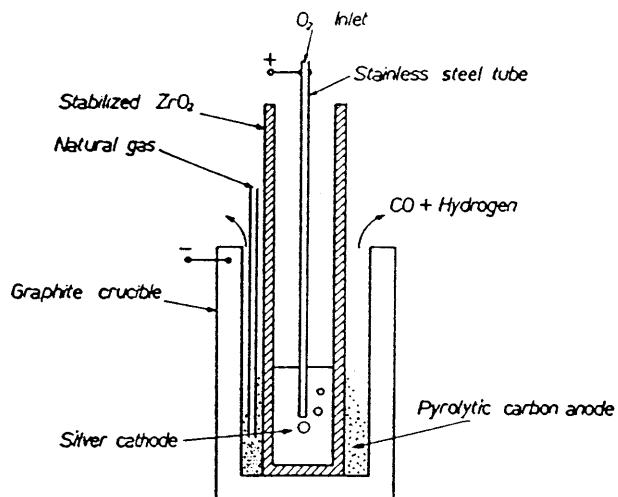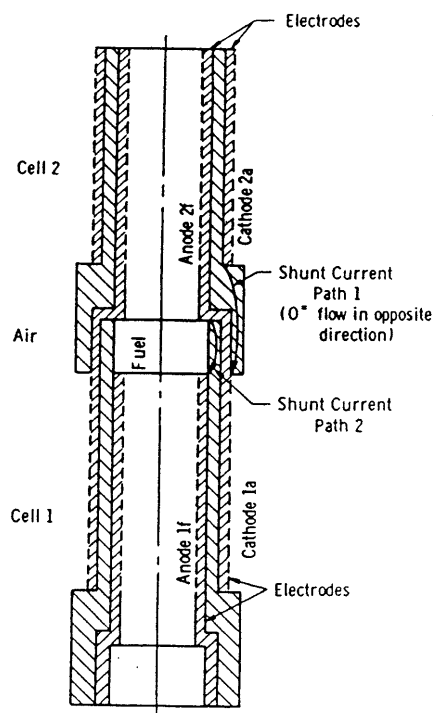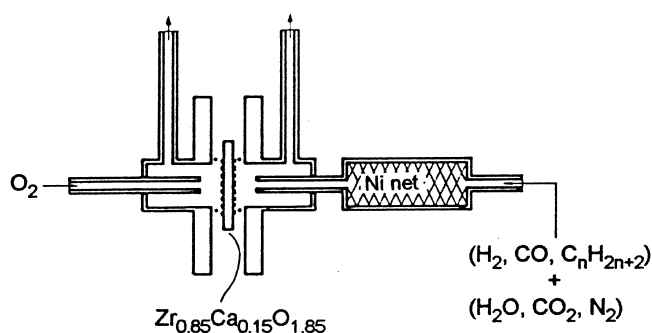

Fig. 7 Cross section of two solid electrolyte fuel cells of the bell-and-spigot type with shunt current paths in the seal region developed at Westinghouse Electric by Archer et al. (1962/64) [52, 53]

current loading; they tended to come loose from the electrolyte and peeled off, probably due to the water vapour formed.

In Europe, Palguyev and Volchenkova published conductivity measurements on the "Problem of solid electrolytes for fuel cells" in 1958, among others for the system 3 $ZrO_2 \cdot 2CeO_2$ + 10 mass-% CaO [88]. From 1960 onwards, results of a broadly based research program on cells with oxidic solid electrolytes appeared at a steady rate from the Ural branch of the Academy of Sciences of the USSR [89] (under the leadership of Karpachov). Tannenberger, who started in 1959 in the Battelle Institute in Geneva (H. Tannenberger, private communication), presented in a patent filed in May 1962 the idea of solid oxide fuel cells consisting of a porous ceramic material as a carrier and thin layers of the cathode, electrolyte and anode upon this carrier [90]. From the Battelle Institute in Frankfurt, Sandstede reported in September 1962 in Rome on the electrochemical oxidation of hydrocarbons by means of a converter upstream of a solid electrolyte fuel cell model [91] (Fig. 8). In December 1962, Kleitz presented in France his first contribution concerning a zirconia fuel cell $Ag-O_2/graphite$ (J. Besson, C. Deportes, M. Kleitz (1962) 1er Colloque sur les piles à combustible. Bellevue, 6 déc. Contrat de recherches 61 FR 136, private communication) [92]. In the first British patent on the subject, filed in August 1963 [93], it was intended to form fuel cells by depositing layers on a porous metallic carrier. In Japan, Takahashi, after investigations with

Fig. 6 Pyrolytic carbon anode fuel cell with zirconia electrolyte crucible investigated at General Electric by Tragert (1961) [80, 103]

Fig. 8 Schematic diagram of the solid electrolyte fuel cell with converter investigated at Battelle Institute, Frankfurt, by Binder et al. (1962) [91]

alkali carbonate electrolytes, published in 1964 his first results obtained on fuel cells with oxidic solid electrolytes [94].

Most developments were started with conductivity measurements for optimizing the solid electrolytes. Some very expensive rare earths, especially ytterbium oxide, were used [95] to achieve highest conductivities, and ternary systems (ZrO_2-Y_2O_3-Yb_2O_3 [96], ZrO_2-Y_2O_3-MgO [97]) were investigated to cut down the costs. As a rule, Al_2O_3 was added to achieve gastight sintering products [95–98]. As early as 1963, the effect of grain boundary conductivity was investigated [99], and the decrease of conductivity with time was seen as a sign of aging of the oxide ion conductors, caused by disorder-order transitions in which the statistical distribution of the cations and oxide ions in the lattice changed to an ordered state [100, 101]. Alterations of the composition influence the effect substantially [102].

Surveys of the activities started were carried out by the international fuel cell meetings in 1965, 1967 and 1969 in Brussels. There, results on solid oxide fuel cells were published in 1965 by General Electric [103], from the Battelle-Institut in Geneva, [66, 104] and from the Universities of Grenoble [105], Nagoya [106] and Greifswald [79].

First investigations of polarisation phenomena in solid oxide fuel cells were delivered by the research groups in Swerdlowsk [89, 109], Frankfurt [91], Grenoble [105] and Nagoya [106]. Fuel cells with cerium-lanthanum mixed oxides were investigated in detail by Takahashi et al. [106] after some earlier investigations [46, 88]. The polarisation phenomena observed were much smaller at the anode than at the cathode or with CaO-stabilized ZrO_2 at anode and cathode. At the anode, by partial reduction of the solid electrolyte, a mixed conductor (solid solution of Ce_2O_3 in CeO_2) and with this an electrode with depolarising interlayer was formed. The electronic transition of the solid electrolyte $Ce_{0.6}La_{0.4}O_{1.8}$ used in an $O_2/H_2,H_2O$ cell in the range 600–1000°C was admittedly between 12 and 22%. Bauerle was the first to investigate the polarisation of solid electrolyte cells in depth by determining the complex admittance method in 1969 [110].

The mobility of the oxide ions in $Zr_{0.85}Ca_{0.15}O_{1.85}$ was determined using $^{18}O/^{16}O$ isotope exchange between solid and gas phase by Kingery et al. in 1959 [111] and more precisely by Simpson and Carter in 1965 [112]. The method extended by Steele et al. [113] to further materials for solid oxide fuel cells serves today for the clarification of fundamental questions of electrode processes, such as exchange current density and electrocatalysis.

The development of electrode materials has always been the focal point of work on solid oxide fuel cells. For the problem of poor adhesion of the anode layers, which became obvious in 1963 [52], Spacil as early as 1964 found the now well-known solution of using layers of nickel closely mixed with solid electrolyte material [114].

It was considerably more difficult to find a suitable cathode material. Indium oxide with different additives was proposed in 1966 [115] and frequently used (e. g. [116–118]). An optimized material with the polyvalent uranium ions in mixed oxides with fluorite structure suitable for sintering on solid oxide electrolytes without phase boundaries was developed by Tannenberger in 1967 [119, 120]. It has proved to be a favourable

Fig. 9a, b Solid oxide fuel cell concepts with flat-plate designs. **a** Shaped disks in a battery proposal of Brown, Boveri by Baukal (1965) [107]. **b** Flat disks between shaped junctions in a battery proposal from the University of Grenoble by Deportes et al. (1967) [108]
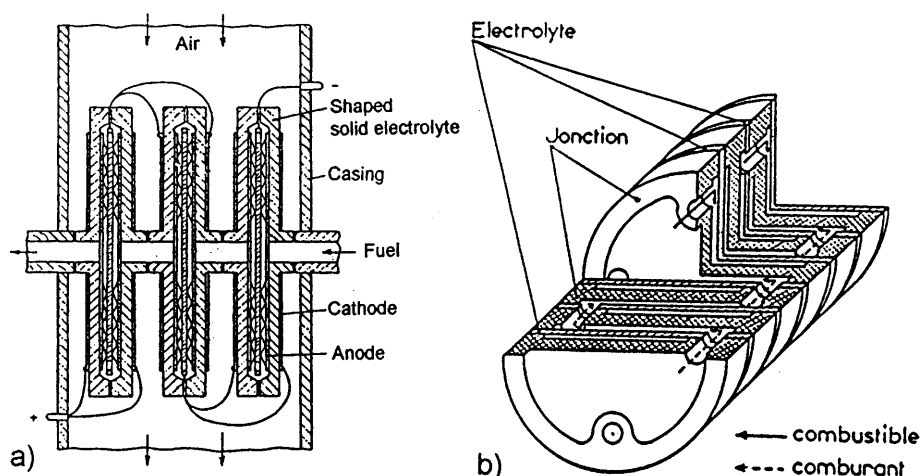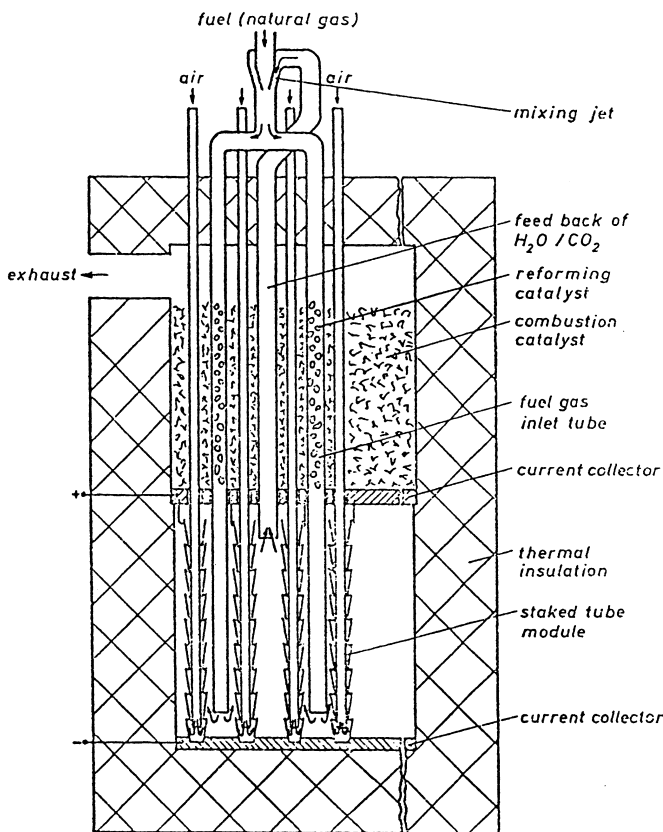
Fig. 10 High temperature fuel cell system for the conversion of methane of Brown, Boveri (1972) [126, 127]

Fig. 11 Review of proposals for connecting self-supporting tubular solid electrolyte fuel cells electrically in series 1974 [130]

interlayer in cathodes and anodes [117, 118]. For the development of cathodes and materials for the connection of electrodes in batteries the introduction of the oxidic electronic conductors with perovskite structure is of particular importance. The development of $La_{1-x}Sr_xCoO_3$ for the air electrode of solid oxide fuel cells marked the beginning [121], and this was followed in 1967 by the recommendation of $PrCoO_3$ [122] and of mixtures of the oxides of Pr, Cr, Ni and Co [123]. But as late as 1969 it was noted in a review [124] that: "It is apparent that a fully satisfactory air electrode for high-temperature zirconia electrolyte fuel cells is still lacking."

From 1964, solid electrolyte fuel cells and oxygen sensors were investigated in the research laboratories of Brown Boveri under the leadership of ROHR (F.J. Rohr, private communication), and in this work between 1969 and 1973 more than 100 oxidic substances were synthesised and tested for their usability [125]. $LaNiO_3$ doped with Bi_2O_3 and $LaMnO_3$ doped with SrO proved to be particularly suitable, and from 1973 $La_{0.84}Sr_{0.16}MnO_3$ was used exclusively (Fig. 10). Admittedly, manganese oxide had already been named in 1962 as a particularly suitable cathode material on zirconia solid electrolytes [86], but only in the perowskite compound has it become the most important material for cathodes so far.
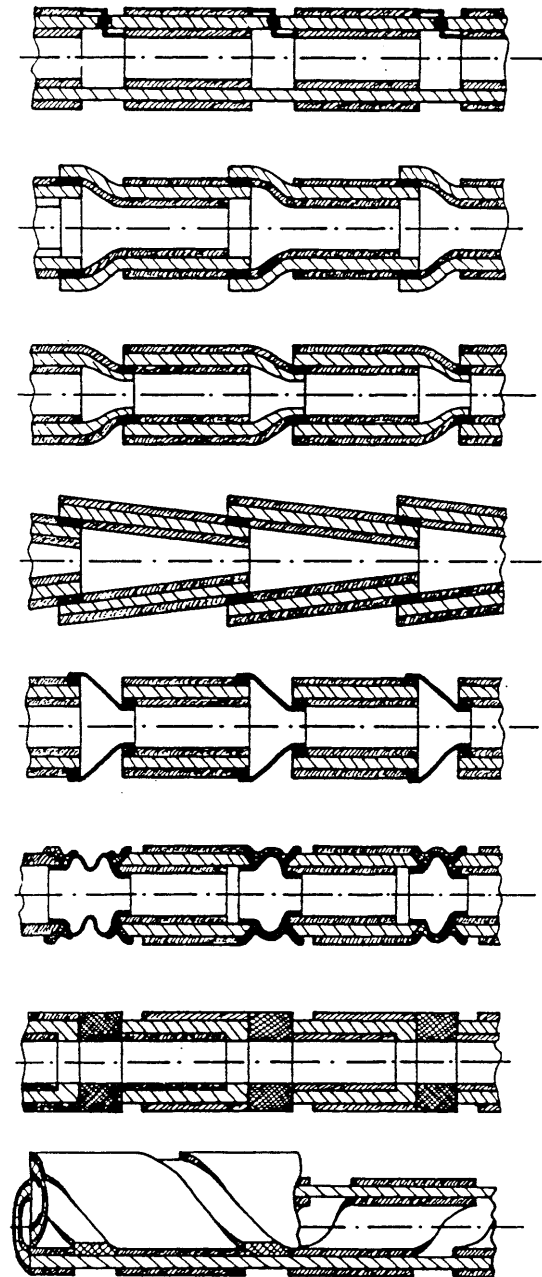
For the electrodes of oxygen generators [128] in investigations started in 1971, $GdCoO_3$ from the series of cobaltates of the rare earths was chosen [129], which forms no low-conductivity layers during the sintering process onto zirconia, has a considerably better conductivity than lanthanum-strontium manganite, and can serve for the direct connection of the electrodes of the same kind in oxygen generators.

In the construction of solid electrolyte fuel cell batteries, two basic forms have been used up to now: tubular cells (see Figs. 2, 4–7, and 10–12), which are more

Fig. 12a, b Westinghouse generator constructed of solid oxide fuel cells of tubular geometry. **a** Perspective sketch showing the five components of a single cell (1982) [131]. **b** Multi-cell generator module design concept [133]
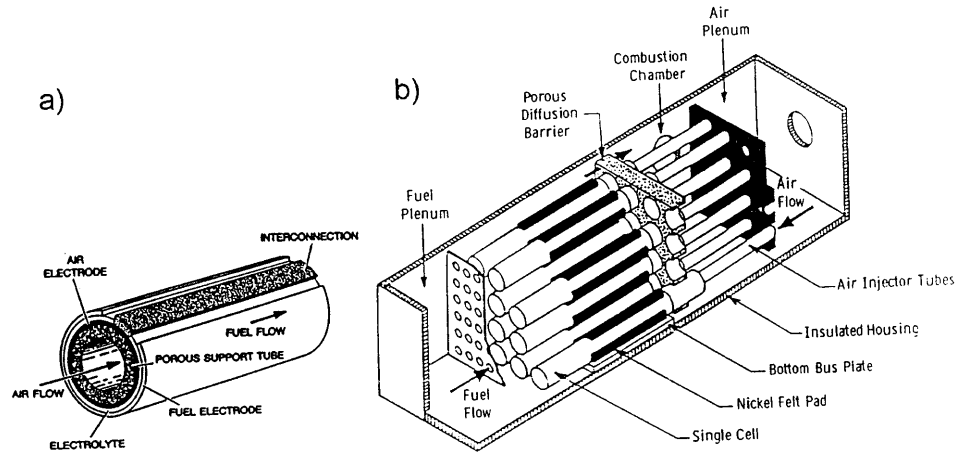
Fig. 13a, b Flat solid electrolyte fuel cell stacks with cross-flow design. **a** Corrugated monolithic fuel cell array of the Argonne National Laboratory containing alternate fuel and air layers rotated 90° with respect to that shown in the figure (1986) [134]. **b** Planar stack concept of Dornier (1991) [135]
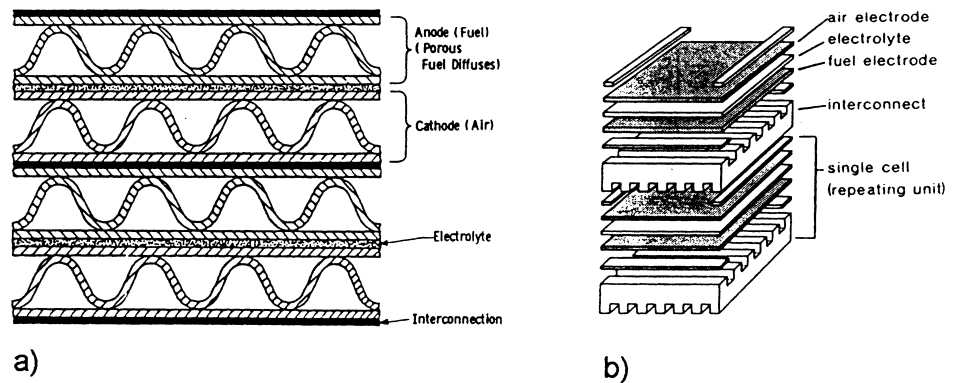
Fig. 14a, b Sulzer HEXIS (**h**eat **ex**changer **i**ntegrated **s**tack) SOFC system initiated in 1991 [136]. **a** Cross section of a five-cell stack. **b** HEXIS 1-kW thermally self-sustaining system containing 40 cells
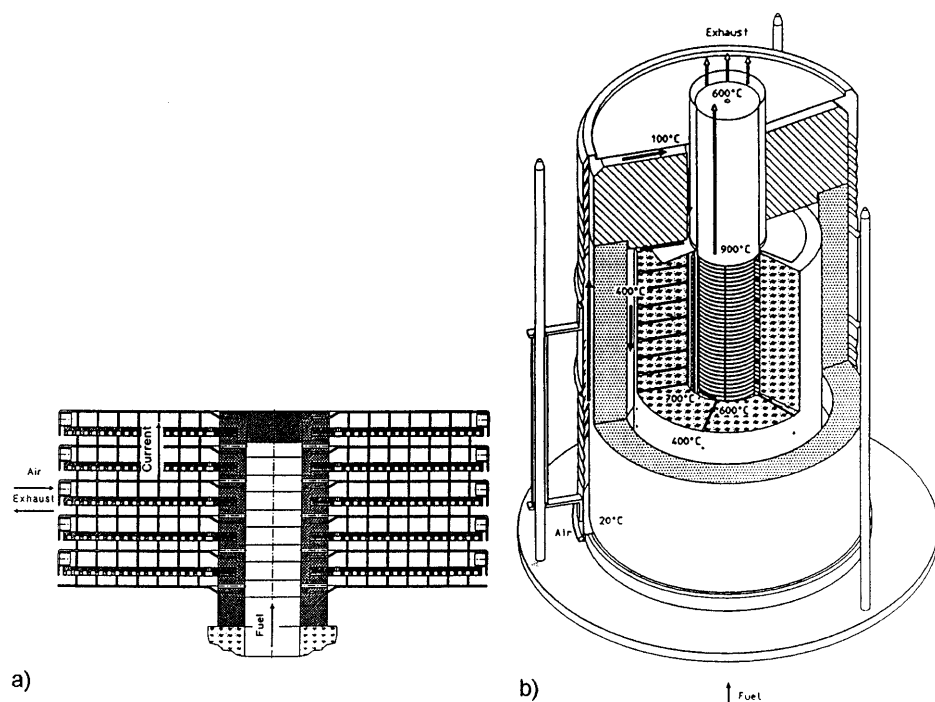
stable against mechanical and thermal stress, and planar cells (see Figs. 3, 8, 9, 13, and 14), which seem to be considerably more fragile. A remarkable stepforward was the development from 1970 by Isenberg of the method of EVD (**e**lectrochemical **v**apour **d**eposition) [132], which is used in the preparation of Westinghouse cells (Fig. 12) for the perfect closing of the pores in solid electrolyte and interconnecting layers.

The connection of fuel cells in series to form batteries, which at first was carried out by soldering, was often attempted (and as it is possible in the case of oxygen generators) by mere overlapping of the anode and cathode of consecutive cells (see for example [137, 138]). Only gradually did it become clear that the interconnecting material, which has to be a good electronic conductor and withstand both oxidizing and reducing gases for prolonged periods, is an indispensable component of batteries of solid electrolyte fuel cells [139]. Most often the development of interconnections is aimed at an oxide ceramic material, and frequently lanthanum-strontium chromite, already described in detail in 1969 [140], is modified. However, particularly for planar concepts (see for example Fig. 14), special metallic materials, already considered in 1967 [141] are also used, e. g. the alloys of chromium with 5% Fe and 1% Y_2O_3 [142].

Already by 1970 the results of investigations on electrical properties and possibilities of the application of solid oxide electrolytes were so numerous as to make them very difficult to survey. A comprehensive review by Etsell and Flengas includes 674 references [143]. Thus, within a relatively short time, the basis was established on which the broad technologically orientated development of solid oxide fuel cells proceeds today.

Conclusion

A first version of the history of solid electrolyte fuel cells was presented by the author at the Second European Solid Oxide Fuel Cell Forum, May 6–10, 1996 in Oslo with the request for discussion and supplementation. Now a revised treatise is submitted, aimed at the focal points and pioneering work in the development of the fundamentals, essentially up to 1970. The direction of developments in recent years could be indicated only briefly.

Appendix

Report of a session of the Academy of Science on Monday, 17 October 1853
C.R. Séances Acad. Sciences (Paris) 37 (1853) 584–588
Physics – Communication about a new class of gas cells
Member J.-M. Gaugain

In a previous communication (Comptes Rendus, session of 18 July 1853), I announced that a source of electricity is obtained by bringing into contact two tubes of glass at high temperature, in which one contains air and the other alcohol vapour, and I observed that the electricity produced in this arrangement can be attributed neither to the transfer of heat nor to the combustion; today I am reporting to the Academy researches made by me to determine the actual cause of the generation of this electricity.

First I will describe a series of experiments which prove that the new source of electricity possesses all essential properties of an aqueous-electrical cell.

1. If an aqueous-electrical cell is brought into contact with a capacitor, then it is sufficient to maintain the connection for one moment to reach the maximum charge tolerated by the capacitor and the cell; I have ascertained that the gas cell *air/alcohol vapour* also possesses the property of charging the capacitor immediately.
2. If different capacitors are brought into contact with an aqueous-electrical cell successively, the quantities of electricity provided by the cell are proportional to the areas of the capacitors, or, at least, increase with these areas; this property can be ascertained easily by means of a leaf electroscope, about which I reported to the Academy recently. This instrument, being based on the property we are dealing with, is applicable with success only if the investigated source shows this property; if it were not the case, the use of the large auxiliary capacitor would reduce the final charge of the electroscope. Concerning the gas cell *air/alcohol vapour*, there is an enormous difference between the obtained performances, depending on whether the auxiliary capacitor is used or one of the tubes is connected directly with the capacitor of the electroscope; in the first case the charge is much greater than in the second case: the *air/alcohol vapour* cell exhibits, as the aqueous-electrical cells, the specific property of delivering a quantity of electricity which is proportional (or approximately proportional) to the capacitor area with which it is brought into contact.
3. When several aqueous-electrical cells are connected with their terminals of contrary signs, and when the battery so formed is brought into contact with a capacitor, the charge obtained increases with the number of cells; I have observed that three *air/alcohol vapour* cells in series give to a capacitor a stronger charge than a single cell.
4. Furthermore, when the terminals of an aqueous-electrical cell are connected by means of a metallic wire, this wire acquires the ability to induce a magnetic deflection; I have ascertained that an *air/alcohol vapour* cell in a closed circuit is also capable of delivering a current easily detectable with a galvanometer.

Because of these observations, I believe that the source of electricity which is the subject of this communication is to be considered as a cell of a special kind; the principle of its action remains to be determined. To do this I have carried out a great number of experiments; I will concentrate on results which seem to me to be the most conclusive.

First, I noticed that the platinum wire serving to bring the tubes into contact with the earth or with a capacitor is replaceable by a wire of gold, silver, copper or iron without changing the results. From this, it can be deduced that the wires in the tubes only play the role of conductors; this conclusion is the most probable because, if the metallic wires were contributing to the production of electricity, it would be difficult to understand why such different metals as platinum and iron behave in the same way.

The metallic wires being simple conductors, the next question to be answered is: do the two gases contribute to the development of electricity. For the clarification of the question I assembled a row of gas cells with air, oxygen, nitrogen, carbon dioxide, hydrogen, water vapour, ether vapour and alcohol vapour, and investigated these cells in the same way as the *air/alcohol vapour* cell. Ether and water were placed, like alcohol, in a tube only closed at one end; the other substances, which are gaseous at room temperature, were enclosed in tubes sealed at both ends, with an electrical connection between the inside of the tube and the outside established by means of a fine platinum wire crossing the sealed part; here are the results I obtained:

The *air/oxygen* cell gives no trace of electricity; all cells which were assembled by combining gases other than air and oxygen give no electrical generation either. On the other hand, when one part is exposed to air or oxygen and the other to any of the gases enumerated above, the cell behaves exactly like the *air/alcohol vapour* cell. Oxygen always produces positive electricity and the other gas negative electricity; the charge of the capacitor seems to be the same whatever gas is combined with oxygen.

When oxygen is mixed with another gas and when oxygen is fairly concentrated, the mixture behaves as air or pure oxygen; but when the oxygen concentration is very small, e.g. one hundredth, then the mixture is "resinous" (negative) with respect to air or pure oxgen and "vitreous" (positive) with respect to a gas free of oxygen.

The conclusion which seems to result from all these experimental facts is that the electricity originates exclusively from the action exercised between oxygen and glass, and that the gas in the second tube only plays the role of a carrying gas; if the second gas were contributing to the production of electricity, it would seem strange that substances as different as water, alcohol, carbon dioxide, hydrogen and nitrogen lead to identical results.

All my experiments were carried out with tubes of glass, but I observed that the experiment by the Member of the Academy Becquerel which prompted my investigations also works well with a tube of porcelain, and I have no doubts that this substance can replace the glass in all cases.

In all the investigations reported I used my leaf electroscope; with this instrument all the experiments which I have described can be repeated very easily whatever the atmosphere and without any drastic precautions.

Other experiments, which I cannot report because of lack of space, confirm all the views expressed above; however, there is one amongst them that first seemed in contradiction, and for this reason I will report it. When two tubes equally filled with air are brought into contact, one connected with the earth by means of a platinum wire and the other with the capacitor by means of an iron wire well polished to remove any corrosion products, a very strong charge of "resinous" (negative) electricity is obtained; if this experiment is repeated several times with the same iron wire, the charges obtained decrease until no signs of electricity are observed when the oxidation has reached a certain extent. At first sight, this experiment seems to prove that the combination of iron with oxygen produces electricity, but here are new observations showing that this interpretation is erroneous:

1. If oxidation were the cause of the observed electricity, then the same results would be obtained with metallic wires in the same tube at a small distance from each other. I made sure with the same leaf electroscope that it is impossible with this arrangement to get any trace of electricity.
2. If oxidation were the cause of the development of electricity, the surface of the iron wire would be the surface where the "vitreous" (positive) and "resinous" (negative) electricities separate, whereas in reality this occurs on the surface of the tube containing the iron wire. Indeed if the wire referred to is not brought in connection with the capacitor but is left isolated in its tube, and if a connection is established between this tube and the capacitor by means of a platinum wire not touching the iron wire, a charge with "resinous" (negative) electricity is obtained as good as if the iron wire itself were connected with the capacitor.

These observations show clearly that the oxidation of iron is not (at least directly) the cause of the observed electricity; it seems to me that this cause resides in the change in the composition of the gas enclosed in the small space separating the glass from the iron wire. As long as the oxidation lasts, the surface of the glass located in the immediate neighbourhood of iron is in contact with nearly pure nitrogen, so that in reality it works as an N_2/O_2 cell; at first this interpretation might seem singular, but here is an experiment demonstrating its appropriateness. I said above that the charges of "resinous" (negative) electricity delivered from the tube which contains the iron wire disappear when iron gets fully oxidized: this occurs when the tube is open; but when the tube is sealed at both ends and is so narrow that it is nearly completely filled by the iron wire, the electricity production does not stop when iron is oxidized but persists indefinitely. This result can be explained, I think, only with the assumption made by me that the electricity is generated by the modification that the combustion of iron induces in the surrounding gas. This modification comes to an end when the tube is open, but remains permanently when the tube is closed. This last analysis confirms the views expressed above about the action principle of the gas cell.

Special terms used by the translator to give better understanding by a modern reader:

Hydro-electrique	Aqueous-electrical
Couple gazeux	Gas cell
Électroscope á double condensation;	Leaf electroscope
Conducteur (gaseux)	Carrier gas
Fluide élastique, fluide	Gas
Acide carbonique	Carbon dioxide
Az-O	N_2/O_2
"resinous" electricity	Negative electricity
"vitreous" electricity	Positive electricity

References

1. Davy H (1807) Elektrochemische Untersuchungen, Vorlesung am 19.11.1807, Verfahrensarten, um die feuerbeständigen Alkalien zu zersetzen. In: Ostwald W (ed) Ostwalds Klassiker der exakten Naturwissenschaften, Nr 45, Leipzig 1893, pp 52–55
2. Faraday M (1833) Experimental-Untersuchungen über Elektrizität, IV. Reihe. Über ein neues Gesetz der Elektrizitätsleitung. In: Oettingen AJ von (ed) Ostwalds Klassiker der exakten Naturwissenschaften, Nr 86, Leipzig 1897, pp 39–55 and Note 9 of the Editor
3. Faraday M (1834) Experimental-Untersuchungen über Elektrizität, VII. Reihe. Von der elektrochemischen Zersetzung. In: Oettingen AJ von (ed) Ostwalds Klassiker der exakten Naturwissenschaften, Nr 87, Leipzig 1897, pp 39–106
4. Erman P (1806) Über die fünffache Verschiedenheit der Körper in Rücksicht auf galvanisches Leitungsvermögen. Ann Physik (Ed Gilbert LW) 22:14–50
5. Hittorf W (1851) Über das elektrische Leitungsvermögen des Schwefelsilbers und Halbschwefelkupfers. Ann Physik u Chem 84: 1–28
6. Buff H (1855) Über die Zersetzung des Wassers durch sehr schwache elektrische Ströme, insbesondere durch die Maschinen-Electricität. Ann Chem Pharm 96: 257–286, especially p 286
7. Cavendish H (1774) Franklin exper and observ, 5th edn, London, p 411; cited from [16]
8. Beetz W (1854) Über die Leitungsfähigkeit für Electricität, welche Isolatoren durch Temperatur-Erhöhung annehmen. Ann Physik u Chem 92: 452–466
9. Buff H (1854) Über die elektrische Leitfähigkeit des erhitzten Glases. Ann Chem Pharm 90: 257–283

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10. Gaugain J-M (1853) Note sur les signes électriques attribués au mouvement de la chaleur. C R Séances Acad Sciences 37: 82–84
11. Becquerel AC (1854) Note sur la production des courants pyroélectriques. C R Séances Acad Sciences 38: 905–910
12. Buff H (1851) Über die elektrische Beschaffenheit der Flamme. Ann Chem Pharm 80: 1–16
13. Gaugain J-M (1853) Note sur une classe nouvelle de couples gazeux. C R Séances Acad Sciences 37: 584–588
14. Warburg E (1884) Über die Electrolyse des festen Glases. Ann Physik u Chem NF 21: 622–646
15. Ohm GS (1830) Schweigg Journ 59: 385, 60: 32 (cited from [14])
16. Wiedemann G (1893/98) Die Lehre von der Electricität 2nd edn, Vieweg u Sohn, Braunschweig, vol I, pp 553–561, pp 815–819; vol II, pp 491–493
17. Ostwald W (1885/87 1st edn ... 1917 5th edn) Lehrbuch der Allgemeinen Chemie, Engelmann, Leipzig
18. Nernst W (1899) Verfahren zur Erzeugung von elektrischem Glühlicht. DRP 104 872, filed 6.7.1897
19. Nernst W (1899) Über die elektrolytische Leitung fester Körper bei sehr hohen Temperaturen. Z Elektrochem 6: 41–43
20. Allgemeine Electricitäts-Ges. Berlin (1901) Verfahren zur Herstellung von Glühkörpern aus Metalloxyden für elektrische Glühlampen. DRP 117 031, filed 10.3.1898
21. Nernst W (1901) Material for electric-lamp glowers. US-P 685 730, filed 24.8.1899
22. Baur E, Preis H (1937) Über Brennstoff-Ketten mit Festleitern. Z Elektrochem 43: 727–732
23. Möbius H-H (1965) Die Nernst-Masse, ihre Geschichte und heutige Bedeutung. Naturwissenschaften 52: 529–536
24. Reynolds H (1902) Über die Leitfähigkeit fester Mischungen bei hohen Temperaturen. Ein spezieller Fall der festen Lösungen. Thesis, University of Göttingen
25. Allgemeine Electricitäts-Ges. Berlin (1900) Elektrische Lampe mit Nernstschem Glühkörper. DRP 114 241, filed 8.4.1899
26. Bartel H-G, Scholz G, Scholz F (1983) Die Nernst-Lampe und ihr Erfinder. Z Chem, Leipzig 23: 277–287
27. Wagner C (1943) Über den Mechanismus der elektrischen Stromleitung im Nernststift. Naturwissenschaften 31: 265–268
28. von Helmholtz H (1882/83) Die Thermodynamik chemischer Vorgänge I, II, III. Sitzungsber Akad Wiss Berlin 2.2.1882, 27.7.1882, 31.5.1883. In: Wiss Abhandlungen, Ambrosius Barth, Leipzig, vol 2 (1883) 958–978, 979–992, vol 3 (1895) 92–114
29. Ostwald W (1894) Die wissenschaftliche Elektrochemie der Gegenwart und die technische der Zukunft. Z Elektrochem 1: 81–84, 122–125 ; Z physik Chem 15: 409–421
30. Haber F, Moser A (1905) Das Generatorgas- und das Kohlenelement. Z Elektrochem 11: 593–609
31. Haber F, Fleischmann F (1906) Über die Knallgaskette. 1. Mitt Z anorg Chem 51: 245–288
32. Haber F, Foster GWA (1906) Über die Knallgaskette. 2. Mitt Z anorg Chem 51: 289–314
33. Haber F (1907) Verfahren zur Erzeugung von elektrischer Energie aus Kohle und gasförmigen Brennstoffen. Öster Pat 27 743, filed 5.8.1905
34. Treadwell WD (1916) Über den Sauerstoffdruck einiger Oxyde und die Kohle-Sauerstoffkette bei höherer Temperatur. Z Elektrochem 22: 414–421
35. Baur E, Treadwell WD (1920) Brennstoffelement. DRP 325 783, filed 20.9.1916
36. Baur E, Brunner R (1937) Über die Eisenoxyd-Kathode in der Kohle-Luft-Kette. Z Elektrochem 43: 725–727
37. Baur E, Preis H (1938) Brennstoff-Ketten mit Festleitern. Z Elektrochem 44: 695–698
38. Baur E (1939) Über das Problem der elektromotorischen Verbrennung der Brennstoffe. Brennstoff-Chemie 20: 385–387

39. Baur E (1940) Brennstoffelemente. Ber Ges Kohlentechn 5: 99–110
40. Schottky W (1935) Über stromliefernde Prozesse im Konzentrationsgefälle fester Elektrolyte. Wiss Veröff Siemens-Werke 14, no 2: pp 1–19, and foreword
41. Siemens and Halske AG, Schottky W named as inventor (1937) Zur Stromlieferung geeignetes galvanisches Element bzw. Elementkette. DRP 650 224, filed 6.4.1935
42. Biefeld K (1954) Brennstoffbatterie. DE-P 912 106, filed 27.2.1944
43. Hund F (1951) Anomale Mischkristalle im System ZrO_2 - Y_2O_3. Kristallbau der Nernst-Stifte. Z Elektrochem, angew physik Chem 55: 363–366
44. Engell H-J (1978) Karl Hauffe zum 65. Geburtstag. Ber Bunsenges Phys Chem 82: 351–352
45. Peters H (1953) Untersuchungen der Gitterstruktur und der elektrischen Leitfähigkeit an Mischoxyden vom Fluorittyp. Thesis, University of Rostock
46. Möbius H-H (1958) Theoretische und experimentelle Untersuchungen an Brennstoffelementen mit festen Elektrolyten. Thesis, University of Rostock and Mitteilungsbl Chem Ges DDR (1959) 6: 45–48
47. Ryschkewitsch E (1948) Oxydkeramik der Einstoffsysteme vom Standpunkt der physikalischen Chemie. Springer, Berlin Heidelberg New York
48. Peters H, Möbius H-H (1958) Elektrochemische Untersuchung der Gleichgewichte CO + 0,5 O_2 = CO_2 und C + CO_2 = 2 CO. Z physik Chem, Leipzig 209: 298–309
49. Peters H, Möbius H-H (1961) Verfahren zur Gasanalyse bei erhöhten Temperaturen mit Hilfe galvanischer Festelektrolytelemente. DDR-P 21673, filed 20.5.1958
50. Möbius H-H (1965) Grundlagen der gaspotentiometrische Sauerstoffbestimmung. Z physik Chem, Leipzig 230: 396–412
51. Möbius H-H (1966) Potentiometrische Titrationen oxydabler Gase mit Luft in Festelektrolytzellen. Z physik Chem, Leipzig 231: 209–214
52. Archer DH, Sverdrup EF, English WA, Carlson WG (July 1963) An investigation of solid-electrolyte fuel cells. Tech Doc Rept ASD-TDR-63–448
53. Archer DH, Zahradnik RL, Sverdrup EF, English WA, Elikan L, Alles JJ (1964) Solid electrolyte batteries. 18th Ann Proc Power Sources Conf May 19–21
54. Loos CH (1970) Vorrichtung zur Regelung des Luft-Brennstoff-Verhältnisses in einem Verbrennungsmotor. DE-P 2 010 793, filed 6.3.1970, priority NL 22.3.1969
55. Peters H, Mann G (1959) Elektrochemische Untersuchung des Gleichgewichtes Fe + CO_2 = FeO + CO. Z Elektrochem, Ber Bunsenges physik Chem 63: 244–248
56. Kiukkola K, Wagner C (1957) Measurements on Galvanic Cells Involving Solid Electrolytes. J Electrochem Soc 104: 379–387
57. Weissbart J, Ruka R (1961) Oxygen Gauge. Rev Sci Instr 32: 593–595
58. Möbius H-H, Lang S, Wilms K (1965) Verfahren zur Herstellung galvanischer Festelektrolytzellen für gaspotentiometrische Zwecke. DDR-P 43242, filed 22.5.1964
59. Möbius H-H, Hartung R (1965) Die Prüfung der Sauerstoffdurchlässigkeit feuerfester Materialien bei hohen Temperaturen durch potentiometrische Gasanalyse mit Festelektrolytzellen. Silikattechnik, Berlin 16: 276–280
60. Schmalzried H (1962) Über Zirkondioxyd als Elektrolyt für elektrochemische Untersuchungen bei höheren Temperaturen. Z Elektrochem, Ber Bunsenges physik Chem 66: 572–576
61. Hartung R, Maass R (1981) Zur unteren Begrenzung der Arbeitstemperatur von Festelektrolyt-Sauerstoffsensoren. Z Chem, Leipzig 21: 337–338
62. Möbius H-H, Witzmann H, Harzer D (1963) Untersuchung zur Ionenüberführung einiger Wolframate. Z Chem, Leipzig 3: 157–158

63. Möbius H-H (1962) Über die Sauerstoffionenleitung fester Körper und die unipolare Ionenleitung bei Fluoritstrukturen. Z Chem, Leipzig 2: 100–106
64. Boyce JB, Huberman BA (1979) Superionic conductors: Transitions, stuctures, dynamics. Physics Reports 51: 189–265, especially p 201
65. Dixon JM, LaGrange LD, Merten U, Miller CF, Porter JT (1963) Electrical resistivity of stabilized zirconia at elevated temperatures. J Electrochem Soc 110: 276–280
66. Tannenberger H, Schachner H, Kovacs P (1965) Etude d'électrolytes solides à base d'oxide de zirconium pour piles à combustible. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 19–26
67. Palguev SF, Neuimin AD, Strekalovskij VN (1966) Abhängigkeit der elektrischen Leitfähigkeit fester Oxidlösungen vom Strukturtyp des Fluorits von der Größe des Kationenradius des zugesetzten Oxids. Tr Inst Elektrokhim Akad Nauk SSSR, Uralsk Filial 9: 149–157
68. Chebotin VN, Perfiliev MV (1978) Elektrokhimiya tverdych elektrolytov. Moskva izdatelstvo "Chimiya". Chapter 4.1 pp 125–129
69. Möbius H-H, Witzmann H, Hartung R (1964) Über die Ionenbeweglichkeit in wasserfreiem Natriumsulfid. Z physik Chem, Leipzig 227: 40–55
70. Möbius H-H (1961) Hochtemperaturelektroden für galvanische Festelektrolyzellen, insbesondere für Brennstoffelemente. DDR-P 22030, filed 20.5.1958
71. Möbius H-H (1959) Über Brennstoffelemente. Monatsber Dt Akad Wiss Berlin 1: 34–36
72. Möbius H-H, Müller J (1961) Untersuchung der Kationenbeweglichkeit in hochtemperaturfesten Oxiden und Mischoxiden mit Th-234. Z Chem, Leipzig 1: 377
73. Möbius H-H, Witzmann H, Gerlach D (1964) Untersuchungen zur Kationendiffusion im System $Zr_{0.85}Ca_{0.15}O_{1.85}$. Z Chem, Leipzig 4: 154–155
74. Rhodes WH, Carter RE (1966) Cationic self-diffusion in calcia-stabilized zirconia. J Amer Ceram Soc 49: 244–249
75. Möbius H-H (1969) Beiträge zur Entwicklung von Hochtemperaturbrennstoffelementen mit sauerstoffionenleitenden Festelektrolyten. Wiss Z Univ Rostock, Math-naturwiss Reihe 18: 935–943
76. Möbius H-H, Rohland B (1968) Method of producing fuel cells with solid electrolytes and ceramic oxide electrode layers. US-P 3,377,203, filed 18.11.1964, DDR-P 46 300, filed 27.6.1963
77. Möbius H-H, Rohland B (1966) Über den Einfluß des Elektrodenmaterials auf das Ergebnis von Messungen zur elektrischen Leitfähigkeit fester Elektrolyte. Z Chem, Leipzig 6: 158–159
78. Rohland B, Möbius H-H (1968) Batterien aus Festelektrolytbrennstoffzellen mit Uranoxid-Anodenschichten. Naturwissenschaften 55: 227–228
79. Möbius H-H, Rohland B (1965) Über Probleme der Hochtemperatur-Brennstoffelemente mit sauerstoffionenleitenden Festelektrolyten. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 27–34
80. Tragert WE (1964) Fuel cell. US-P 3,138,487, filed 28.2.1961
81. Tragert WE (1964) Fuel cell. US-P 3,138,488, filed 8.3.1961
82. Tragert WE, Fullman RL, Carter RE (1964) Fuel cell. US-P 3,138,490, filed 28.2.1961
83. Tragert WE (1964) Fuel cell with stabilized zirconia electrolyte and nickel-silver alloy anode. US-P 3,296,030, filed 1.11.1962
84. Oser W (1966) Fuel Cell. US-P 3,281,273, filed 5.5.1961
85. Ruka RJ, Weissbart J (1968) Electrochemical method for separating O_2 from a gas, generating electricity, measuring O_2 partial pressure, and fuel cell. US-P 3,400,054, filed 24.7.1961
86. Bray DT, Lagrange LD, Merten U, Park CD (1967) Fuel cell having zirconia-containing electrolyte and ceramic electrodes. US-P 3,300,344, filed 27.6.1962
87. Weissbart J, Ruka R (1962) A solid electrolyte fuel cell. J Electrochem Soc 109: 723–726
88. Palguyev SF, Volchenkova ZS (1958) Das Problem der festen Elektrolyte für Brennstoffzellen. Tr Inst Khim, Akad Nauk SSSR, Ural Filial, 2: 183–200; C A (1960) 54: 9542 i
89. Karpachov SV, Palguiev SF, Chebotin WN; Neuimin AD, Filiayev AT, Perfiliev MV et al (1960 foll) Tr Inst Elektrokhim Akad Nauk SSSR, Ural Filial, 1 foll
90. Tannenberger H, Schachner H, Simm W (1969) Festelektrolytbrennstoffelement. DE-P 1 471 768, filed 22.5.1963; priority 23.5.1962 Switzerland
91. Binder H, Köhling A, Krupp H, Richter K, Sandstede G (1963) Elektrochemische Oxydation von Kohlenwasserstoffen in einer Festelektrolyt-Brennstoffzelle bei Temperaturen von 900–1000°C. Electrochim Acta 8: 781–793
92. Besson J, Deportes C, Kleitz M (1965) "Étude des électrolytes solides pour piles à combustible à haute température" and "Utilisation des électrolytes dans les piles à combustible à haute température". In: Les piles à combustible. Éditions Technip, Paris, pp 87–102 and 303–323
93. Williams KR, Smith JG (1964) Fuel cell. GB-P 1 049 428, filed 15.8.1963
94. Takahashi T (1966) Research and development of fuel cells in Japan. J Electrochem Soc, Japan 34: 60–69
95. Tannenberger H (1966) Electrolyte solide pour piles à combustible. Suisse-P 400 264, filed 23.11.1962
96. Rohr FJ (1971) Festelektrolyt für Brennstoffzellen. DE-P 1 671 704, filed 18.3.1967
97. Rohland B, Möbius H-H (1988) Leitfähigkeits- und Stabilitätsuntersuchungen an Festelektrolyten für Brennstoffzellen aus dem System ZrO_2-$YO_{1.5}$-MgO. Abh Sächs Akad Wiss, Leipzig, Math-nat Kl 49: 355–366
98. Neumeier U, Tannenberger H (1969) Fester Elektrolyt für Brennstoffelemente. Suisse-P 400 263, filed 23.11.1962. DE-P 1 471 770, filed 22.11.1963
99. Tien TY (1964) Grain boundary conductivity of $Zr_{0.84}Ca_{0.16}O_{1.84}$ ceramics. J Appl Phys 35: 122–124
100. Tien TY, Subbarao E C (1963) X-ray and electrical conductivity study of the fluorite phase in the system ZrO_2-CaO. J Chem Physics 39: 1041–1047
101. Subbarao EC, Sutter PH (1964) Order-disorder and ionic conductivity in cubic ZrO_2-CaO. J Physics Chem Solids 25: 148–150
102. Takahashi T, Suzuki Y (1967) Time dependence of electrical conductivity of stabilized zirconia. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, p 378
103. White DW (1965) A zirconia electrolyte fuel cell. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 10–18
104. Schachner H, Tannenberger H (1965) Comportement d'anodes en nickel dans les piles à combustible à électrolyte solide. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 49–55
105. Kleitz M, Besson J, Deportes C (1965) Les processus élémentaires de la réaction d'électrode à oxygène dans les oxydes électrolytes solides à haute température. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 35–41
106. Takahashi T, Ito K, Iwahara M (1965) The fuel cell with a new type solid electrolyte. Rev Energ Primaire. Journées Int d'Etude Piles à Combustible, Bruxelles, vol 3, pp 42–48
107. Baukal W (1968) Brennstoffbatterie. Schw P 444 243, filed 8.4.1965
108. Deportes C, Besson J, Vitter G (1967) Problèmes soulevés par le fonctionnement de batteries de piles à combustible à oxyde électrolyte solide. Rev Energ Primaire. Journées Int d'Etude des Piles à Combustible, Bruxelles
109. Karpachov SV, Filiayev AT, Palguyev SF (1964) Polarization of carbon monoxide electrodes on platinum in a solid zirconia-lime electrolyte. Electrochim Acta 9: 1681–85
110. Bauerle JE (1969) Study of solid electrolyte polarization by a complex admittance method. J Phys Chem Solids 30: 2657–2670

111. Kingery WD, Pappis J, Doty ME, Hill DC (1959) Oxygen ion mobility in cubic $Zr_{0.85}Ca_{0.15}O_{1.85}$. J Amer Ceram Soc 42: 393–398

112. Simpson LA, Carter RE (1966) Oxygen exchange and diffusion in calcia-stabilized zirconia. GE Report 65-RL-3985 M, June 1965. J Amer Ceram Soc 49: 139–144

113. Steele BCH, Floyd JM (1971) Oxygen self-diffusion and electrical transport properties of nonstoichiometric ceria and ceria solid solutions. Proc Brit Ceram Soc 19: 55–76

114. Spacil HS (1970) Electrical device including nickel-containing stabilized zirconia electrode. US-P 3,503,809, filed 30.10.1964

115. Isenberg A, Pabst W, Sandstede G (1970) Oxydisches Kathodenmaterial für galvanische Brennstoffzellen für hohe Temperaturen. DE-P 1 571 991, filed 22.10.1966

116. Sverdrup EF, Glasser AD, Archer DH (1971) Fuel cell comprising a stabilized zirconium oxide electrolyte and a doped indium or tin oxide cathode. US-P 3,558,360, filed 8.1.1968

117. van den Berghe P, Tannenberger H (1972) Festelektrolyt mit Elektrode. Suisse-P filed 18.6.1971; DE-P 22 28 770, filed 13.6.1972

118. Tannenberger H, van den Berghe P (1976) Festelektrolyt mit Elektrode. Suisse-P filed 19.11.1974; DE-P 25 51 936, filed 19.11.1975

119. Tannenberger H (1969) Électrode pour pile à électrolyte solide. Suisse-P filed 19.7.1967; F-P 1.572.073, filed 18.7.1968

120. Shuk P, Schmidt P, Ruhle R, Jakobs S, Möbius H-H (1984) Eigenschaften des Gemischtleiters $Zr_{0.75}Yb_{0.18}U_{0.07}O_{1.91+\delta}$. Zhem 24: 271–272

121. Button DD, Archer DH (1966) Development of $La_{1-x}Sr_xCoO_3$ air electrodes for solid electrolyte fuel cells. Amer Ceram Soc Washington, Meeting May 1966

122. Mitoff SP (1970) High temperature electrical conductor comprising praseodymium cobaltate. US-P 3,533,849, filed 12.6.1967

123. Pabst W, Sandstede G, Walter G (1971) Sauerstoffelektrode für galvanische Zellen, insbesondere Kathoden in Brennstoffzellen. DE-P 1 671 721, filed 23.12.1967

124. Tedmon jr CS, Spacil HS, Mitoff SP (1969) Cathode material and performance in high-temperature zirconia electrolyte fuel cells. J Electrochem Soc 116: 1170–1175

125. Rohr FJ et al (1977) Entwicklung des Prototyps einer Hochtemperatur-Brennstoffzellen-Batterie. Forschungsabschlußbericht 1976, BMFT-FBT 77–17

126. Steiner R, Rohr FJ, Fischer W (1972) High temperature fuel cell system for the conversion of methane. Rev Energ Primaire. Proc 4th Int Symp Fuel Cells, Antwerpen, Oct 2–3, vol 1 A

127. Fischer W, Kleinschmager H, Rohr FJ, Steiner R, Eysel HH (1972) Hochtemperatur-Brennstoffzellen mit keramischen Elektrolyten zum Umsatz billiger Brennstoffe. Chem Ing Tech 44: 726–732

128. Guth HU, Hartung R, Jakobs S, Möbius H-H, Rohland B (1976) Einrichtung zur elektrochemischen Abtrennung von Sauerstoff aus Luft und Verfahren zur Herstellung der Einrichtung. DDR-PS 119 772, filed June 30, 1975

129. Jakobs S, Hartung R, Möbius H-H, Wilke M (1980) Sauerstoffelektroden aus Mischoxiden mit Zirkondioxid und Cobaltaten der seltenen Erden. Rev Chim minér 17: 283–298

130. Möbius H-H (1974) Zur Entwicklung der Elektrochemie mit Festelektrolyten. Mitteilungsbl Chem Ges DDR 21: 177–182 (On opening the conference "Oxidische Festelektrolyte und ihre Anwendungsmöglichkeiten", Greifswald, Sept 17–19, 1974)

131. Isenberg AO (1982) Recent advancements in solid electrolyte fuel cell technology. Nat Fuel Cell Seminar Abstracts, Nov 14–18, Newport Beach, California

132. Feduska W, Isenberg AO (1983) High temperature solid oxide fuel cell – technical status. J Power Sources 10: 89–102

133. Brown JT (1989) Solid oxide fuel cells. In: Takahashi T (ed) High conductivity solid ionic conductors, Worlds Scient, Singapore, pp 630–663

134. Fee DC et al (1986) Monolithic fuel cell development. Fuel Cell Seminar Tucson, Arizona, Courtesy Associates, Washington, pp 40–43

135. Dönitz W, Erdle E, Schäfer W, Schamm R, Späh R (1991) Status of SOFC development at Dornier. Proc 2nd Int Symp SOFC Athens, Commission Europ Communities, Luxembourg

136. Diethelm R, Honegger K, Batawi E (1994) Status of the Sulzer HEXIS SOFC stack and system development. Proc 1st Europ SOFC Forum Lucerne, Oct 3–7, Bossel U (ed), pp 947–952

137. White DW (1969) Fuel cell with tubular electrodes and solid electrolyte. US-P 3,460,991, filed June 21, 1965

138. Archer DH, Alles JJ, Sverdrup EF (1969) Brennstoffzellenbatterie. DE-P 1 922 970, filed May 6, 1969, US priority May 13, 1968

139. Baukal W, Kuhn W, Kleinschmager H, Rohr FJ (1976) Das Elektrodenverbindungsmaterial, ein zentrales Bauelement in Hochtemperatur-Brennstoffzellen. J Power Sources 1: 91–97, 203–213

140. Meadowcroft DB (1969) Some properties of strontium-doped lanthanum chromite. Brit J Appl Phys 2 (J Phys D) 2: 1225–1233

141. Tedmon CS, White DW (1970) Electrochemical cell including iron-chromium alloy conductor connected to cathode. US-P 3,516,865, filed Aug 30, 1967

142. Quadakkers WJ, Greiner H, Köck W (1994) Metals and alloys for high temperature SOFC application. Proc 1st Europ SOFC Forum Lucerne, Oct 3–7, Bossel U (ed), pp 525–541

143. Etsell TH, Flengas SN (1970) The electrical properties of solid oxide electrolytes. Chem Rev 70: 339–376