THE DEVELOPMENT OF FUEL CELLS

-by-

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Professor George W. Swett
Secretary of the Faculty
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Dear Professor Swett:

I take pleasure in presenting herewith a thesis titled "The Development of fuel cells" written in partial fulfillment of the requirements for a degree of Bachelor of Science in the Department of Chemical Engineering.

Yours sincerely,

Clinton C. Kemp

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I. INTRODUCTION

The source of all energy capable of doing work is the sun. This energy may be used either as soon as it is received, or stored and used later. At this time there are no commercial methods for the immediate use of solar energy. It has become necessay, therefore, to release it from various natural stores, namely oil, wood, and coal. The methods for making the energy available are by combustion under a steam boiler and use of a steam engine, or combustion in an internal combustion engine. Whichever of these methods is used, the completeness of the conversion of the potential energy in the fuel into useful work is severely limited by the Carnot efficiency of such a transformation. For instance, a steam engine operating at 1000°R and using condenser water at 500°R will be capable, in the absence of all other losses such as friction, of converting only 50 per cent of the fuel energy into work. In addition to this limit in efficiency, the boiler used will have a heat efficiency not exceeding 85 per cent. Thus these two factors alone make it impossible to convert more than about 42 per cent of the potential energy in the fuel to useful work. Other losses such as friction come into the picture also and reduce this efficiency to about 25 per cent for the most efficient installations.

These low efficiencies have led to investigations into the possibility of converting the energy in the fuel directly into useful work. The Carnot efficiency is the single largest factor contributing to the high loss in potential energy when a heat engine is used as the work producing agent. The elimination of the stage which involves the conversion of heat into work is,,therefore, an important step forward in the methods for conversion of fuel energy into useful work. The electric cell presents many advantages and does in fact eliminate the heat to work stage in the present boiler steam engine process. The theoretical energy which could be derived from a cell is the sum of the changes in free energy involved in the combustion of the fuel used in the cell. When the cell is operating reversibly in the thermodynamic sense, there would be no energy losses in the system; However, as soon as power is drawn from the cell, the efficiency will fall off from an almost perfect to some lower value. At present, one cell has been designed which will deliver 70 per cent of the fuel's energy(7). Even if lower efficiencies than this are obtained, the cell would still be a major advance in fuel economy providing that it operated a little more efficiently than the steam sets now in operation.

Historically, interest in fuel cells started in 1839 when Grove(11) built a cell operated with two platinum electrodes, air bubbled on one, and water gas from coke bubbled on the other. The cell was not a success. In 1855, Becquerel(10) made a cell of a carbon rod electrode, a platinum electrode, and an electrolyte of fused nitre. This cell was no more successful than the Groves cell. Both these cells have been modified until the latest ones give a current of about 100 milliamps at about 0.7 volts. Polarization is-severe, however, in all these cells. Later work, especially by Emil Baur and collaborators has been conducted with cells of the type carbon:"rigid conductor": passive iron. The "rigid conductor" is in most cases a clay with various rare earth metal oxides mixed into it. These cells operate at about 1000°C. Baur reports(8) that he has constructed a cell of this type which is cheap to construct, efficient, but as yet of undertermined length of life under operating conditions.

Some research is still being done on cells with fused electrolytes, but the main purpose of this work has been the search for and investigation of possible depolarizing agents for the cells(9,25,26).

It seems that at this time the heat of combustion of coal can be turned directly into electric power, but that the process involves expensive, unreliable equipment. The impetus of future research must be directed, therefore, toward better equipment or a new type of cell.

II. SUMMARY

A very considerable amount of work has been done in an attempt to devise a practical fuel cell. All of the cells use fuel oil or coal. It has been suggested that sulfite pulp waste liquor be used as a fuel, or that sulphur would prove to be good one also.

Fuel cells are divided into two general classes. Those which use the fuel directly as one of the electrodes or are used to generate a gas (e.g. water gas) from the fuel and involve gas electrodes; and secondly those which use the fuel to reduce material in the cell and air to reoxidize this same material(26). Both types suffer from excessive polarization, while the first type must be operated at a very high temperature in order to get a reaction rate fast enough to produce energy at a satisfactory rate. The second type also suffers from low reaction rate, but initially at least a fair sized current can be drawn from the cell, however, the reoxidizing reaction is unable to go fast enough to supply the cell the oxidizing agent necessary for its continued operation.

It seems that future research must be directed along three major lines. In the first place, suitable depolarizers must be found which will permit cells to continue in operation for extended periods of time. In the second place, the reaction rates must be increased so that the cells may be operated at lower temperatures. In the third place, the investigation for fuel more suitable than coal or oil must be continued.

Fuel cells are at this time definitely only laboratory curiosities, and cannot yet be considered any where near commercially feasible.

III. DISCUSSION OF THE LITERATURE SURVEY.

Before discussing fuel cells themselves, it is interesting to note that there are several other methods which have been suggested for solving this problem of inefficiency in fuel energy conversion into useful work. Diesel's original plan was to use solid fuel in his engine, and by this means to reduce the losses in energy from the fuel which are normally unavoidable in the boiler and steam supply to an engine or turbine. Thus a well run~~s~~ diesel engine will operate and deliver about 25 per cent of the energy in the fuel, whereas the best steam installations cannot deliver more than about 20 per cent of the potential fuel energy. In 1912, William Ramsay(18) proposed the installation of gas engines which would be operated by water gas on the surface at coal mine shafts. He suggested running two concentric tubes down to the coal bed, igniting the coal electrically, and blowing steam down one of the tubes, and water gas out of the other. According to Ramsay, a conversion of the 30 per cent of the fuel energy to power would be possible. The process does not seem to have any particular advantages in its favor, and it is doubtful if it could be succesfully operated anyway.

Several people have written resumés about the state of the art of converting fuel energy directly into electrical energy(2,20,21,& 27). Rideal and Evans(21) have classified the various fuel cells under three headings which will be used as the basis of this discussion. These categories are as follows:

1. Direct fuel cells wherein the fuel is used directly as one of the electrodes;
2. Semi-direct fuel cells wherein the fuel is used to produce some gas (e.g. water gas) which is used with an inert material as a gas electrode;
3. Indirect fuel cells wherein the oxidized and reduced substances in the cell are regenerated by the use of fuel and air respectively.

A discussion of the characteristics and the development of the various cell classification follows.

A. Direct fuel cells:

It is intended that the overall cell reaction shall be the burning of carbon to carbon dioxide, and the other materials with the carbon (i.e. hydrogen, sulfur, etc) will be burnt to their oxides. The cells usually consist of a carbon or fuel electrode, a suitable electrolyte and ~~a~~ air electrode. Early cells of this type were designed by Becquerel(10), Jablochkoff(20), and Swan(20). The first one used carbon and platinum electrodes, while the second one used carbon and iron electrodes. Both used fused nitre as the electrolyte. The third cell was made of carbon and lead electrodes, with a lead chloride electrolyte. None of these cells were successful. In 1897, Jacques(21) designed a cell using fused caustic soda as the electrolyte, a carbon rod for the negative pole, and passive iron over which air was bubbled for the positive pole. This cell was of doubtful usefulness, even though it was the parent of many later designs, because the caustic soda was converted to carbonate and formate. If the cell was to be used for any length of time, these materials would have to be converted back again to the hydroxide, and thus a very large part of the energy produced would be consumed to no useful external purpose.

It was pointed out by Haber(15) and by Patterson(16) who repeated and expanded Haber's work that the operation of the Jacques cell was not really the direct combustion of carbon, but that in the presence of the molten caustic soda, the carbon reacted with the soda and evolved hydrogen which was responsible in part for the cell operation. Furthermore, it was discovered that the presence of a little manganate was an "essential" impurity for the proper operation of the cell.

In 1910, Taitelbaum(23) reported on a large number of experiments carried out on cells of the Jacques type. He found that materials such as saw dust, sugar, and coal could be used as the negative pole of the cell. However, the cells polarized badly, and hence could deliver no useful current. He later substituted concentrated sulfuric acid for the fused sodium hydroxide of the Jacques cell and carried out further tests. He found that the inclusion of a little vanadium salts in the electrolyte improved the operation of the cell. It was observed that the cell operated most effectively at 250°C, and gave an open circuit voltage of 0.6 volts. When the cell was delivering 0.1 amperes, the polarization was considerable. In addition to these experiments, Taitelbaum also conducted some experiments in which he added various amounts of manganese dioxide to the electrolyte. He found that the manganate present tended to attack the carbon electrode, so he further modified the cell by the inclusion of a porous diaphragm intended to prevent the manganate from getting to the carbon electrode. The results were no more encouraging, however, for the cell still polarized significantly.

Following these experiments, Bechterev(9) worked on the original type of Jacques cell. He found that no current could be obtained in the cell if it was operated at a temperature lower than 500°C. He found that several materials such as sodium carbonate, sodium perchlorate, potassium permanganate, selenium, and tellurium could be used as depolarizing agents. In particular, selenium was found to be very active for the carbon electrode in caustic soda. When the electrolyte was boiling, he reports an electromotive force of 0.9 volts. However, he found that if boric anhydride was used as the electrolyte, and platinum as the positive pole, electromotive forces of better than one volt could be obtained at high temperatures if various oxides of the iron or copper groups for instance were added to the electrolyte. He does not report what currents could be obtained. However, by comparison with the later cells it seems likely that no large current could be obtained, and the voltage would drop to well below one volt on the passage of a current.

Baur and Ehrenberg(1) modified this boric anhydride cell of Bechterev by the use of a fused silver positive electrode instead of the platinum. Oxygen was supplied to this electrode. At 1000°C the cells furnished about 0.1 amperes at a half volt. These workers tried various other electrolytes including silicates, carbonates, and fluorides.

Reed(19) developed another cell of this general type. He used fused borax as the electrolyte, and added manganese dioxide to it. The negative pole was broken coal, which floated on the surface of the borax. Imbedded in the coal was a graphite grid which served as the terminal for the pole. Strips of gold foil were used as the positive pole. He describes the advantages of the gold electrode as being the fact that it floats on the electrolyte and thus is self adjusting to position and immersion, and furthermore, he says it favors oxidation of the manganese by the air at the surface of the electrolyte. He prevented the graphite rod from getting into contact with the electrolyte and the fuel gas coming off the cell by piling a sufficient quantity of coal onto the fused borax to protect it. He separated the cell into an oxidation region and a reduction region by a refractory wall which dipped into the molten electrolyte, but did not quite reach the bottom of the cell. Both parts of the cell were closed, provision being made for the evolution of the combustion gases and recharging the coal into the reduction region, and for the supply of air to the oxidation region. The oxidation of the coal takes place by the reduction of the manganese dioxide, which is reoxidized at the gold electrode. The voltage was about 0.9 volts and delivered initially a current of about 0.18 amperes which fell off after an hour to 0.16 amperes. The cell had to be operated at about 950°C. It has the distinction of being the first cell of this type which worked reasonably well. However, a large quantity of heat would have to be expended in order to keep the cell hot. Furthermore, it is not certain that the rate of reoxidation of the manganese dioxide could be made to keep pace with its reduction in the cell. Nothing has been done in later years on cells of the Reed type.

In 1922, Baur, Treadwell and Trümpler(3) described a cell made of a magnesium oxide crucible set in a larger iron crucible. The space between the crucibles was filled with a mixture of coke and fused sodium carbonate. The inside of the magnesium oxide crucible was filled with iron wire and rust, through which air was blown. The cell was somewhat modified by Gregor(13) who obtained a British patent in 1933 on a cell fitted with a magnesium oxide diaphragm, and using iron and carbon electrodes with fused carbonates of the alkali and alkaline earth metals as the electrolyte. The cell was certainly not good enough for commercial operation.

In 1935, Tamaru with Ochiai(24) and later with Kamada(25) published some results of investigations they had carried out on the depolarization of various of the fuel cells already described. They tested a cell in which carbon was the cathode, and copper and copper oxide the anode. Alkali carbonates and halides were used for the electrolyte. They found that the polarization could be eliminated by the addition of salts of manganese and boron which served as oxygen carriers. The overall reaction was the combustion of carbon. In the later paper(25) they state that the cells will not operate below red heat because the reaction rate is too slow, and depolarization too difficult to obtain. They found that the voltage developed was independent of both the air rate and the oxygen content of the air flowing past the copper electrode.

Von Rhorer(28) checks these results closely with a cell of this carbon copper copper oxide type. He found, however, that if the electrolyte was thickened with magnesia and lime, the air to the copper electrode could be controlled satisfactorally and side reactions prevented. He states that the voltages obtained remained constant for days. Polarization was said to be only a few hundredths of a volt. At an operating temperature of 863°C, the voltage was 1.072 volts. However, an energy balance showed that only 13 to 18 per cent of the energy of the reaction of carbon to carbon monoxide was produced usefully. Internal resistance counted for 10 per cent and side reactions for 35 per cent of the energy.

This type of cell, namely a carbon electrode, fused electrolyte, and an ~~iar~~ air electrode has been modified in two cases. Fischer and König(12) tested the voltage of cells with aqueous sodium carbonate as the electrolyte when operated under pressure. They found that their best results were obtained when solid fuels were used for one of the electrodes rather than liquid fuels. They also discovered that lignites were unsuitable fuels because their reactions involved the production of humic acids which apparently "poisoned" the cell. They found that current could be drawn but had considerable difficulty in the design of the apparatus.

The other major modifications of this type of cell are due to Baur and his many collaborators. Thus he and Preis(4) tested the resistance of various diaphragms in 1937, and found that the inclusion of various of the rare earth oxides into clay gave the best results. They called these mixes "rigid conductors" and Baur and Brunner(5) concluded later in the same year that the successful way to build a fuel cell was to keep it completely dry (i.e. use no fused electrolyte). They found that cells of this type, carbon-"rigid conductor"-ferric oxide air electrode were very simple to construct but had high internal resistance. In 1939, however, Baur and Preis(6) reported that using a diaphragm of composition one part ceric oxide, one part lithium zirconate, four parts clay, and three parts tungston trioxide, a cell of one to two ohms internal resistance could be made to deliver an~~d~~ electromotive force of 0.7 volts. Baur reports(7) that these cells must be operated at about 1000°C and that under these conditions develop about 70 per cent of the

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theoretical voltage. In 1941, Baur[8] reported a successful cell constructed on this rigid conductor principle but using hydrogen gas as the fuel. It therefore falls in the second type of fuel cells and will be described there.

It may be said that the operation of cells of the first class are severely hampered by polarization on the one hand, and the necessity for operating at excessively high temperatures on the other. Research in this field must be confined at present to the search for depolarizers, and perhaps catalysts or faster reacting oxygen carriers which will increase the cell reaction rate sufficiently to permit operation of the cells at temperatures below 1000°C. It would seem that these present cells consume so much energy in the form of heat to keep at the high temperature necessary and have such high internal resistance that they are not very efficient in operation, and in fact probably no better than the present internal combustion engine or boiler installations.

B. Semi-direct fuel cells:

Cells of this type are operated by converting the fuel into a gaseous material such as carbon monoxide in a producer gas set. These gases are bubbled over metal cathodes. Many cells of this type have been developed, however, they are from the start less efficient than the direct cells for some of the fuel energy is consumed in the gasification operation. This energy is liberated as heat and could no doubt be used to some extent, but some loss is inevitable.

Grove constructed the first cells of this type when he used two platinum electrodes saturated with hydrogen and oxygen respectively. The development of a suitable voltage in these cells is difficult because of the senstitiveness of the hydrogen electrode. Mond(20,21) experimented with water gas as a gas for the cathode. However, he accidentally discovered nickel carbonyl in the course of his experiments, and became more interested in the purification of nickel than the perfection of a fuel cell. He separated two platinum electrodes coated with platinum black by a porous diaphragm. The electrolyte was dilute sulfuric acid. He obtained a current of about 2 amperes at 0.7 volts. However there was so much platinum in the cell that its cost was prohibitive, and in addition, it was found difficult to keep the platinum black saturated with the oxygen and the hydrogen. Seigl attempted to make the cell less costly by suspending the carbon black on small pellets of carbon, but experienced considerable trouble in keeping the electrodes saturated with the gases.

Baur and Ehrenberg(1) describe the use of hydrogen with their molten silver cathode cell. Their important contribution was the fact that metals of the iron and copper groups could be used in place of platinum for the electrodes. Later (1921) Baur in collaboration with Treadwell(2) constructed a cell using producer gas with a diaphragm of prismatic structure of fritted magnesia.

This diaphragm was said to serve as a wick for the molten sodium and potassium carbonates used as the electrolyte. The apparatus was maintained at 800°C. It is reported that this cell was not badly polarized, and had a capacity of about one K. W. per cubic meter. They state that for economy the units must be at least one thousand K. W. capacity, and may use regenerative heating because the gases are only 70 per cent burnt in the cell. By this means, the authors claim an 80 per cent heat economy. The overall cell would return about 60 per cent of the fuel energy as electricity. German patents (325,783 and 325,784 of 1920) and a British patent (126,766 of 1919) were taken out on the cell.

In 1934, a gas cell of this general type was patented in this country by Gregor(14). Very few details on its operation are available except to the effect that it operates at about 700°C. The most recent published account of a gas cell, however, comes from Baur(8). He has built a number of cells with diaphragms as solid conductors as described earlier(7). He mounted these cells in troughs and fed the electrodes with hydrogen and oxygen. The cells are small enough so that 25,000 of them may be mounted in a cubic meter. He says that the cost of the plant installation is small, but does not know how well the cells will stand up when in use.

The overall picture of the indirect cells is not very clear. It seems that they are subject to polarization just as much as the direct cells. They must also be operated at high temperatures. The cells can be operated by the use of platinum electrodes, but become prohibitively expensive to install. If some other metal could be found which would replace platinum, then the cells might prove successful. However some metals have been tried as substitutes but no successful results have been obtained(21). The Baur cell is apparently very complicated and of boudtful durability.

C. Indirect fuel cells:

In cells of this type, a typical one being the Jungner cell, ~~in which~~ two carbon electrodes are used. They are separated by a porous diaphragm and immersed in sulfuric acid. Air is bubbled over the anode, and fuel over the cathode. An oxygen carrier is used in the cathode chamber such as nitric oxide as originally proposed by Jungner, or vanadium salts as suggested by Taitelbaum(23). Cells of this type are said to produce voltages of about 0.6 volts, but can deliver only very small currents.

The operation of these cells is limited by the rate at which the fuel can be oxidized, and the rate at which the oxygen carrier (nitric oxide, vanadium salts, etc.) can be reoxidized by the air at the cathode. Polarization is also a major stumbling block in these cells.

A general survey of the entire field would show that the major problem is probably polarization and the rate of reaction. If some method can be developed which will cause the reaction rates to go up, then the cells may be operated at a very much lower temperature. This will result in a saving of fuel used for heating the equipment, and also easier construction. Cells of the indirect type have an advantage in that they may be operated with an aqueous electrolyte and at room temperature or slightly above. However the cells polarize with time due to the slowness of regeneration of the oxygen carrier. It would be fair to state that at this time the conversion of fuel energy directly into electrical is a laboratory curiosity but is far from practical as a commercial proposition. Of course, it may prove advisable to turn to some other form of fuel than coal or oil. Thus Schwabe(22) suggests the use of the waste sulfite pulp liquor. In attempts to oxidize the liquor in a cell, it was found that the reaction rate was very slow. However Schwabe estimates that in Germany alone there are $2x10^9$ K.W. lost annually in this potential power source. Sulfur may prove to be a better fuel, however, so far as can be determined from the literature, no one has done any work on it.

IV. CONCLUSIONS

1. The conversion of fuel energy directly into electrical energy is at this time a laboratory curiosity only, and is far from a practical solution for commercial use.

2. In order to get rapid enough reaction rates in the cells, direct and semi-direct fuel cells must be operated at high temperatures.

3. Low temperature indirect fuel cells have been designed, however, they suffer from the low rate at which the oxygen carriers are reoxidized.

4. Polarization is a major problem to be met and solved in all types of fuel cells.

5. Investigations into other types of fuels may prove the best road to the successful construction of a fuel cell.

6. Development of depolarizers are essential if the present cell types are to prove successful.

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