A REVIVAL OF FUEL CELL TECHNOLOGIES ?

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A Quarter Century Summary paper published 1978 in the Journal of the Electrochemical Society [1] describes the rapid development of the main Fuel Cell Systems after 1950, the Alkaline Fuel Cell efforts starting with Bacon and leading to the Apollo Moon and Space Systems. The ground work leading to the molten carbonate and solid oxide fuel cells of today and the beginnings of the acidic systems with the phosphoric fuel cells. Hydrazine as fuel was researched by nearly all companies in the fuel cell business until it was stopped as "poisonous". And during these years the development of the Polymer Electrolyte Fuel Cells, beginning with General Electrics Gemini cells tried to get to the top. Over one dozen very informative books on Fuel Cell Technologies were written between 1960 and 1973. [1]. An excellent, technologically specific historic survey can be made from the 1956 – 72 Annual United States Army Proceedings [1] and all the following Biannual Power Sources Conferences (next in June 2002).

After 1975, Fuel Cells were getting much lower attention. The main reason was that they were seen as an expensive uneconomic energy source in view of low-cost competition (oil, gas). Many Space and US-Government contracts disappeared due to budget cuts. Fuel Cells were only reviewed [2]. This changed about 1990, when Fuel Cells became interesting again. The outlook statement in the 1976 paper was right: Another Fuel Cell wave came, based on material and system improvements, increased environmental concerns and changed investor spirits [3].

Fuel Cells with Polymer Electrolyte Membranes had improved, they are suggested for electric vehicles, but the economy of using them is still not assured, the system costs are too high. Would it help to go back to the classic system with alkaline electrolyte and consider its revival? In a project at the Technical University Graz, supported by Electric Auto Corp., Ft. Lauderdale, FL, considerable improvements in the electrode performance have been achieved by new catalysts and designs [4]. All the AFC accessories, pumps, heat exchangers, etc., are low-cost. Liquefied ammonia was chosen as hydrogen source, it is easily cracked in an inexpensive 500 deg. C cracker, at a high efficiency. Ammonia was also a fuel source in the US-Army and early fuel cell technology [1]. It is also worldwide available, can be made from air-nitrogen and hydrogen produced with energy from renewable sources like water-, sun- and wind power via water electrolysis.

Direct Methanol Fuel Cells (DMFCs) have been developed, as electrolyte they use Polymer Electrolyte Membranes (PEMs) which are acidic in nature, therefore the air electrode polarization is relatively high. The authors of this paper work also in this field and try to improve the performance by adding an acidic circulating electrolyte to the membrane system, thereby reducing the cross-leakage of the methanol towards the air cathode, which damages the catalyst. The surprising results of combining PEMs with circulating electrolytes are not limited to DMFCs. The circulating electrolyte can also be used for heat management and water transport control in PEM hydrogen fuel cells.[5]. This concept, which is used in a project with Energy Vision, Inc., Ottawa, Canada, in cooperation with the National Research Council and the Alberta Research Council has been progressing well.

It was only a matter of time to look also at the Alkaline Methanol-Air Cell possibilities. A screening of the classical fuel cell literature was very helpful [6].

Question: Can methanol-air cells replace metal-air cells ?

.The use of Zinc-Air and Zinc-Aluminum cells with exchangeable electrolyte and replaceable metallic anodes has been suggested for many purposes, ranging from military power sources to electronic equipment to electric vehicles. However, the re-installation of anodic plates in series connected batteries is rather complicated. To solve this problem, a circulating alkaline electrolyte containing powder zinc was used in a vehicle already demonstrated in 1971 by Sony [3]. Unfortunately, but not surprisingly, it suffered from pump failures.

But there are also good features: The use of an alkaline electrolyte assures a high level performance of the air cathodes, even with non-noble metal catalysts. Then, instead of electrically recharging the anodes of the system, new Zinc metal and fresh electrolyte was again supplied. In later versions, Zn-metal pellets and dry KOH powder mixes were inserted and only water had to be added. All these procedures are mechanical in nature and not too efficient if the energy needed for the regeneration is considered. In 1994 a large project using Zn and ZnO in replaceable cassettes was supported by the German postal service [7]. It was finally abandoned, but recently a Zinc-Air Bus demonstration was done in Las Vegas again.

The mechanical features are avoided by using a methanol-caustic liquid electrolyte as energy source. The used up, partly carbonated electrolyte is exchanged. This is not new either [1] and current densities up to 2 A/sqcm have been reported [6], with only one major trouble: the cross-leakage of the methanol to the air cathode destroys the noble metal catalysts. Asbestos barrier layers were used in the old systems. The remedy is: use selective air catalysts (insensitive to methanol). In a classical, five cell battery demonstrator "Fuelectric", Allis Chalmers added methanol and hydrogen peroxide to the electrolyte and used selective catalysts, Pt for methanol and Ag for the air side. Or, to use very effective membranes and circulating electrolytes with residual methanol elimination, like in the acidic system [5]. Work of that kind is done in Graz.

Summary and Outlook

The classical "old" fuel cell literature reveals many good features which can be utilized in modern systems. Fuel cell and battery hybrid history is also worth studying [7].

References

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