

## Introductory Lecture: Principle and Applications of Fuel Cells (Methanol/Air as Example)

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### 1. Conversion of Chemical Energy into Electricity

The energy of a chemical reaction depends only on the difference in energy of the reacting species before and after the complete reaction. Different pathways are possible, e.g. purely chemical or purely electrochemical routes. The chemical reaction proceeds in a homogeneous reaction volume as the combustion of gasoline or alcohol with oxygen. The energy obtained is a combination of mechanical energy and heat. *Electrochemical pathways* are proceeding at two different electrochemical interfaces, anode and cathode, separated by an ion conducting electrolyte. The total reaction takes place in an electrochemical cell, the fuel cell. Fig. 1 shows as an example the reaction of methanol with air or oxygen in a Direct Methanol Fuel Cell (DMFC).

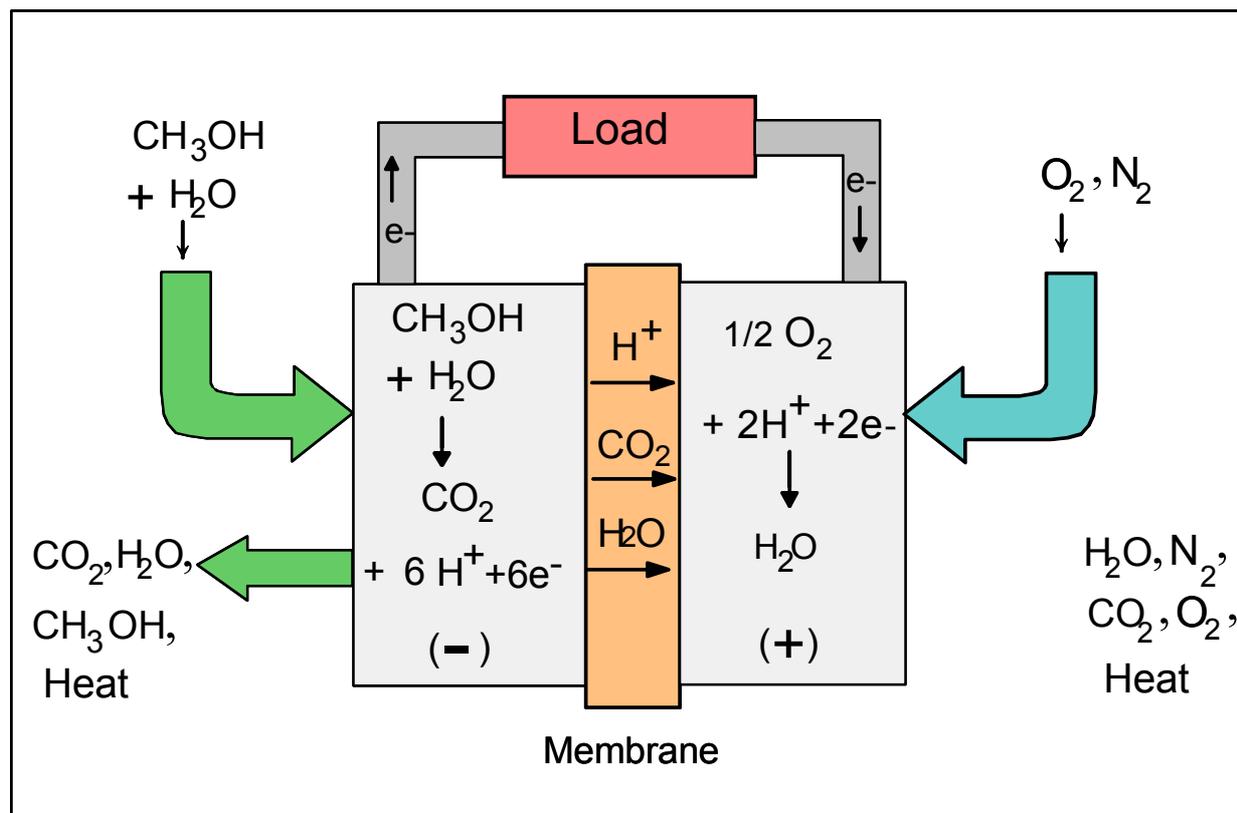
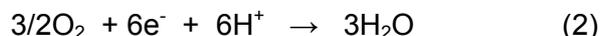


Fig. 1: Flow of reactants, water,  $\text{CO}_2$  and heat in the case of a Direct Methanol Fuel Cell (DMFC).

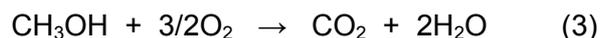
Methanol and water are circulated at the gas side of the anode interface. Protons formed move through the polymer electrolyte together with water and the reaction product CO<sub>2</sub>:



The electrons, moving via the load resistance, react at the cathode interface with oxygen:



Summing up equations (1) and (2), one has as the total chemical reaction:



With the direct electrochemical reaction of methanol, the power is given by the product cell voltage times current,  $E_{\text{cell}} \times I = \text{watts (volt} \times \text{amperes)}$ , and the energy obtained after a certain time can be calculated by the product volt x Ah = Wh. With a complete reaction 6 electrons per molecule of methanol are obtained. Assuming the maximum possible (reversible) cell voltage of 1.21V for a methanol/air cell as well as 6 electrons per molecule of methanol, the respective energy amounts to 6kWh per kg methanol. This energy content is comparable to the one of gasoline [1, 2].

## 2. Activity of Fuel Cell Electrodes

The standard free energy of reaction (1) is  $\Delta G = -692.2 \text{ kJ/mol}$ . From this follows for a 6 electron charge transfer the thermodynamic standard cell voltage of 1.21V [2]. But, in a practical cell, we have to consider the reaction kinetic of both electrodes and the IR drop in the electrolyte.

A first view on the reaction kinetics can be obtained via cyclic voltammograms (CV), using selected electrode materials [1, 3]. Fig. 2 presents the well known cyclic voltammogram for methanol at a platinum electrode in acid solution. The CV for hydrogen is given for comparison. An important information is, that at platinum the oxidation of methanol does *not* start at the thermodynamic data near the hydrogen potential in the same electrolyte at ca. +20mV, but above 400mV (note the arrow for a change of potential in the positive direction). What are the possible reasons?

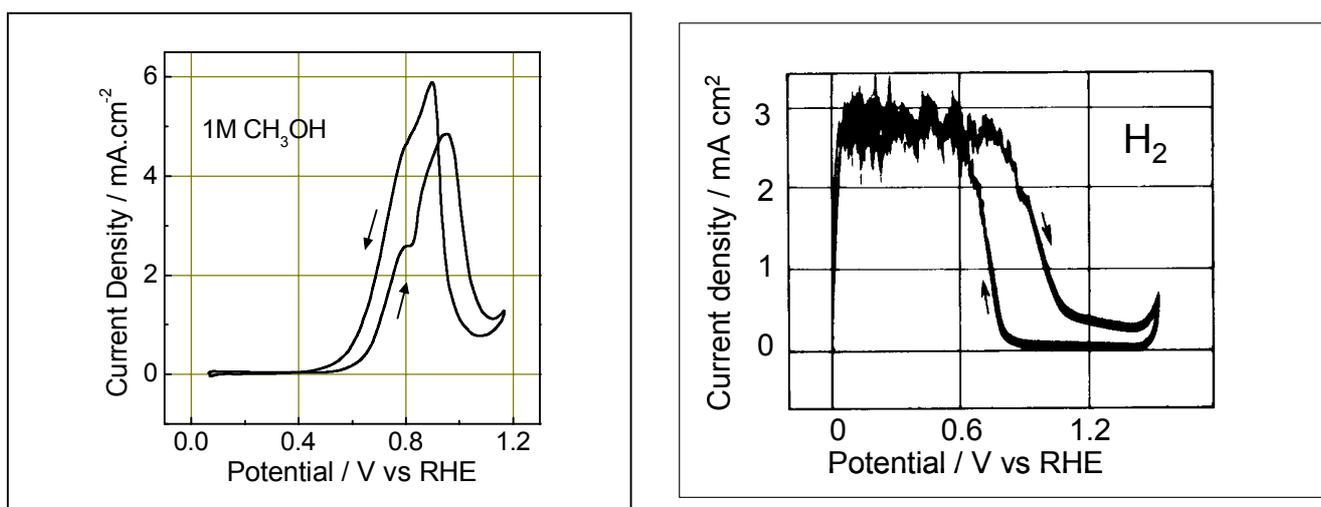
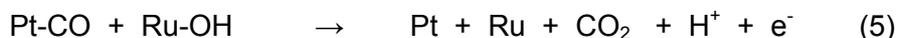
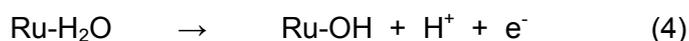


Fig. 2: Cyclic Voltammogram for methanol on porous platinum in 1M HClO<sub>4</sub> and for H<sub>2</sub> on smooth polycrystalline Pt in 0.5M H<sub>2</sub>SO<sub>4</sub> for comparison, scan of electrode potential 50mV/s, 20°C [3].

It is more than a decade that Kunimatsu did find, by analysis of insitu IR spectra, in CH<sub>3</sub>OH/H<sub>2</sub>SO<sub>4</sub> solution on platinum surfaces at 400mV RHE bands for linearly bonded CO. Improving the IR technique, Iwasita obtained in addition spectra with bands of bridge bonded and multi bonded CO, with bands of COH and HCOOCH<sub>3</sub>. HCOOCH<sub>3</sub> is a product of the solution reaction of HCOOH with methanol. It has to be considered that in addition to the reaction path via CO to CO<sub>2</sub>, formic acid and formaldehyde are formed as intermediates in solution [4]. Finally, formic acid and formaldehyde are also oxidized to CO<sub>2</sub> at the electrode, that is, all the three pathways of methanol oxidation result in 6 electrons per molecule.

An important step in electrocatalysis was the observation that the rate of methanol oxidation is increased in replacing pure platinum as a catalyst by the use of PtRu alloys. Due to the above observation that CO is an adsorbed intermediate, and due to the fact that the oxidation of CO requires a second oxygen atom, and Ru is splitting water at low potentials easier than Pt, the following bifunctional mechanism was assumed:



From this model about the mechanism it is to be expected that the distribution of Ru and Pt sites in the surface of the catalyst must be a sensible factor for improving the catalyst activity.

### 3. The 40W DMFC System from Smartfuelcell, Brunenthal (Germany)

The oxidation of methanol in acid electrolyte, as in the DMFC of Fig. 1, has the advantage that according to equation (3) two molecules of water are formed per molecule of methanol. This fact supports the closed system operation where sufficient water has to be introduced in the fuel compartment, together with methanol. The 40 watt unit of Fig. 3 is using its electronic device for controlling the flow of methanol and air, for circulating water and for the adjustment of the operating temperature, at e.g. 60<sup>o</sup> C, including respective heat balance regulations [5]. In addition, the control device takes care for the exhaust of the final product CO<sub>2</sub>. An example of the remarkable long time performance is given in Fig. 4.

In future, liquid methanol, or possibly also *ethanol*, could be a basis not only of the stand by applications of today, but for new mobile units also. For this type of application, we have to wait for new ideas in the development of respective electrocatalysts, in order to increase cell voltage and cell power.

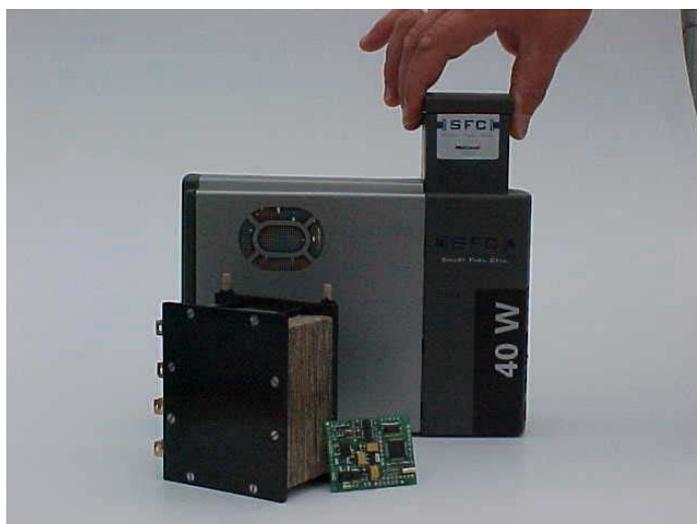


Fig. 3: 40 Watt PEM DMFC fuel cell system of Smartfuelcells, Brunenthal/ Germany, working at ambient air, 200mA/cm<sup>2</sup> at 400mV cell voltage, 12 volt stabilized, 60<sup>o</sup>C, 1 mg/cm<sup>2</sup> PtRu (50:50), cell stack and electronic card in front, 2.5 l methanol container in the box, obtainable energy 1 Wh/cm<sup>3</sup> methanol [5].

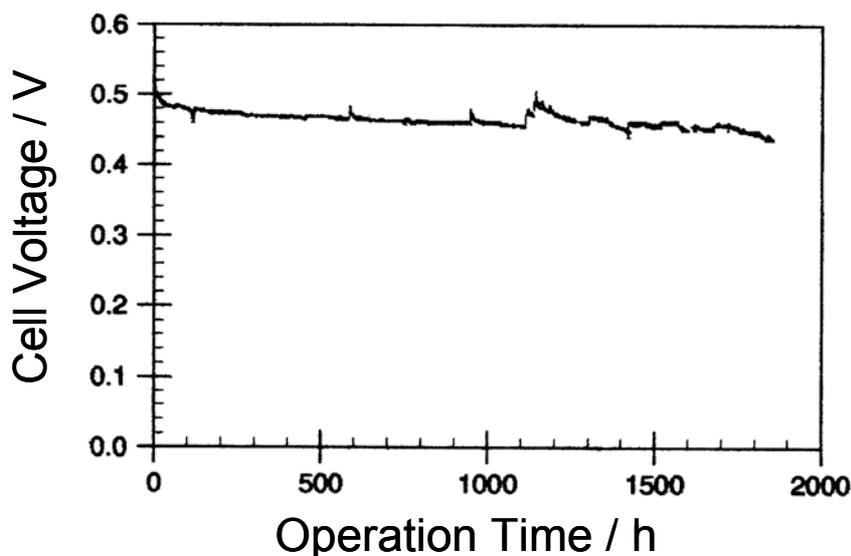


Fig. 4: Lifetime performance of Smartfuelcell methanol electrodes in 0.4M CH<sub>3</sub>OH at 200mA/cm<sup>2</sup> and 110°C, degradation rate 13μV/h [5].

#### 4. Outlook

During recent years, special progress was obtained in three areas:

- (1) Volume and weight of cell stacks for hydrogen/oxygen (air) was decreased using very thin Nafion membranes (100 to 20μ) as proton conducting electrolyte, at the same time minimizing the thickness of the catalyst layer of Pt nano-particles and optimizing the gas distribution over the electrode interfaces at temperatures near 100°C.
- (2) Complete hydrogen systems, including gas and water circulation, of 1kW to 200kW were build with automatic control of fuel (oxygen) stoichiometry and stack (fuel, oxygen) temperature. The good data in power density do allow the application as power sources in vehicles also.
- (3) Beside the hydrogen system, the Direct Methanol Fuel Cell was developed for temperatures of 60-90 degree with a similar technology as discussed above, but approaching a more simple system due to higher content of water as reaction product. On the basis of present catalysts (mainly PtRu bicatalysts for the methanol anode) an acceptable power per active surface is available, and a use in smaller systems from some watts to 1kW for several mobile and stationary application is suggested.

Important fields for future studies are:

Reducing the system costs, especially taking care for the development of new membranes with sufficient life time data as well as using less amounts of platinum metal catalysts.

Renewed investigation of alkaline systems as an alternative option, using non-noble metal catalysts and a simplified technology.

Other alcohols than methanol like ethanol or glycol should be studied also as a possible fuel for liquid-fuel fuel cells. Here, the study of suitable catalysts is still in an early stage. Key for a possible break-through is the development of a catalyst for the direct pathway of oxidation to CO<sub>2</sub>. In the case of using platinum metal catalysts, the kinetics of the first steps of oxidation to acetaldehyde or acetic acid are already comparable to the kinetic of methanol oxidation.

## References

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