What can muSR do for fuel cells?

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Whereas the 19th Century was the century of the steam engine and the 20th Century was the century of the internal combustion engine, it is likely that the 21st Century will be the century of the fuel cell.

Outline

- Why fuel cells and Hydrogen energy?
- How fuel cell works
- Direct methanol fuel cell and muSR
- Conclusion

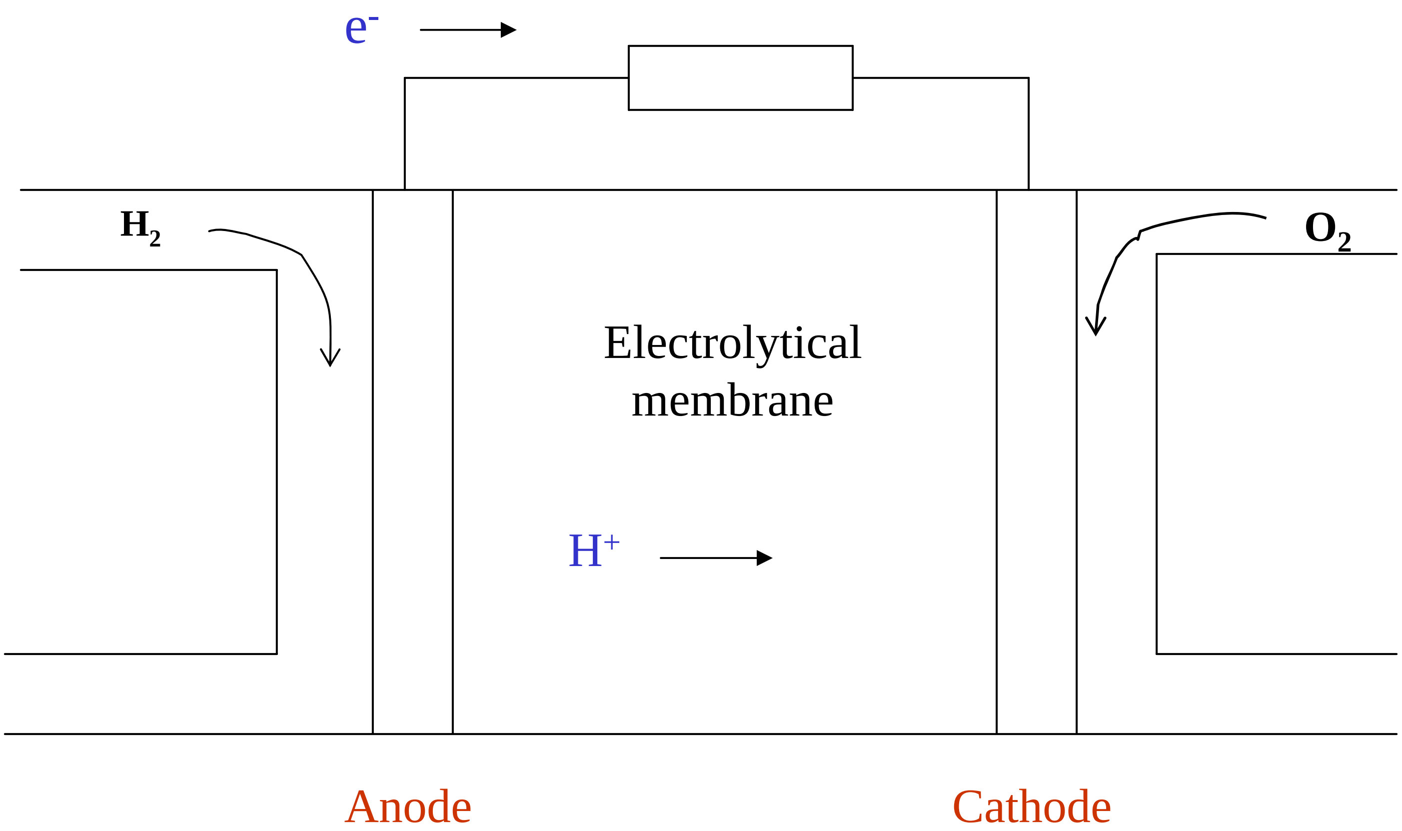
Why fuel cells and Hydrogen energy?

1. The hotbed effect - climate change. Main pollutant – cars, about 50% of CO_2
2. Supplies of fossile fuels are limited. Some experts expect that during next 100 years the fossile fuels can be depleted.
3. Extraction of enormous amounts of substance from the deep of the Earth can change the dynamic equilibrium in thermal and mass transport within the Earth. Nobody knows that it can provoke?

Hydrogen is produced from the water and is converted to the water!

Efficiency: internal combustion engine – 30%, fuel cells - 70%

How fuel cell works?



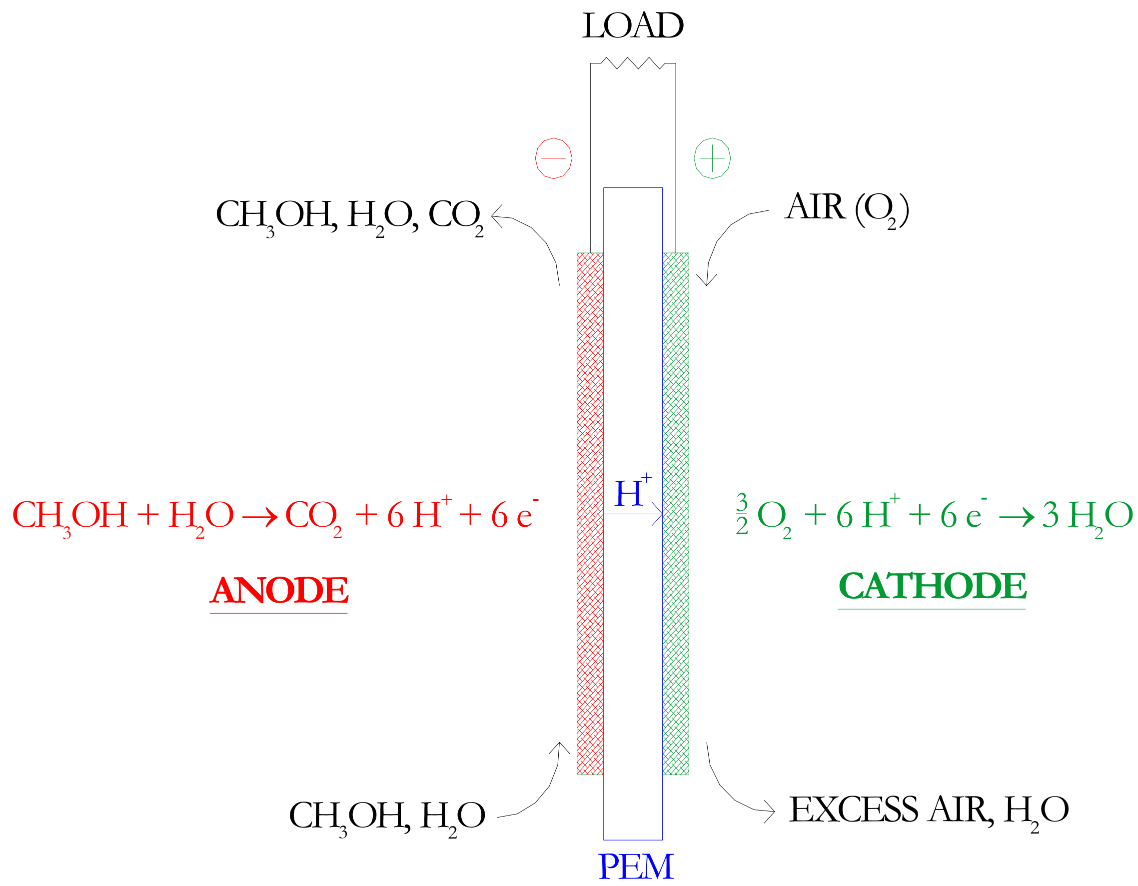
Reaction: $H_2 = 2H^+ + 2e^-$

$O_2 + 4H^+ + 4e^- = 2H_2O$

$J = 200 – 500\ mA/cm^2$, $V = 0.6 – 0.8\ V$

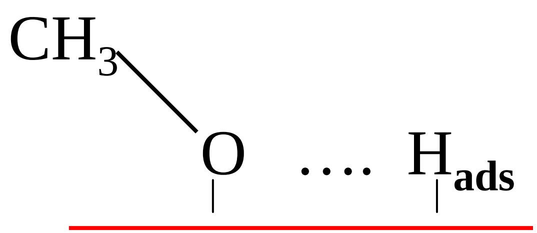
H_2 – difficulties with storage, transportation; Methanol – liquid – easy to store

DMFC OPERATIONAL SCHEMATIC



Reaction steps of CH_3OH decomposition on carbon supported Pt nanoparticles

$$\mathbf{CH_3 - OH \rightarrow CH_3 - O \rightarrow H_2C{=}O \rightarrow CO \rightarrow C{=}O_2 + H_2}$$



Catalyst surface

How one can get the information concerning the organic compounds by means of muSR?

Mu, which is an indispensable precursor of all reactions with organic compounds undergoes the following chemical reactions:

- abstraction: $Mu + CH_3OH \rightarrow CH_3O + MuH$ (1)
- radical combination: $Mu + \bullet OH \rightarrow MuOH$ (2)
- addition: $Mu + (CH_3)_2C{=}O \rightarrow (CH_3)_2C\bullet - OMu$ (3)

In reactions 1,2 the muon ends up in diamagnetic environment and gives rise to a precession frequency corresponding 13.55 kHz/G. Reaction 3 describes the formation of muonium-substituted radical.

$(CH_3)_2C\bullet - OMu$

In muonium substituted radical, the unpaired electron is also coupled to the adjacent magnetic nuclei, as well as to the muon.

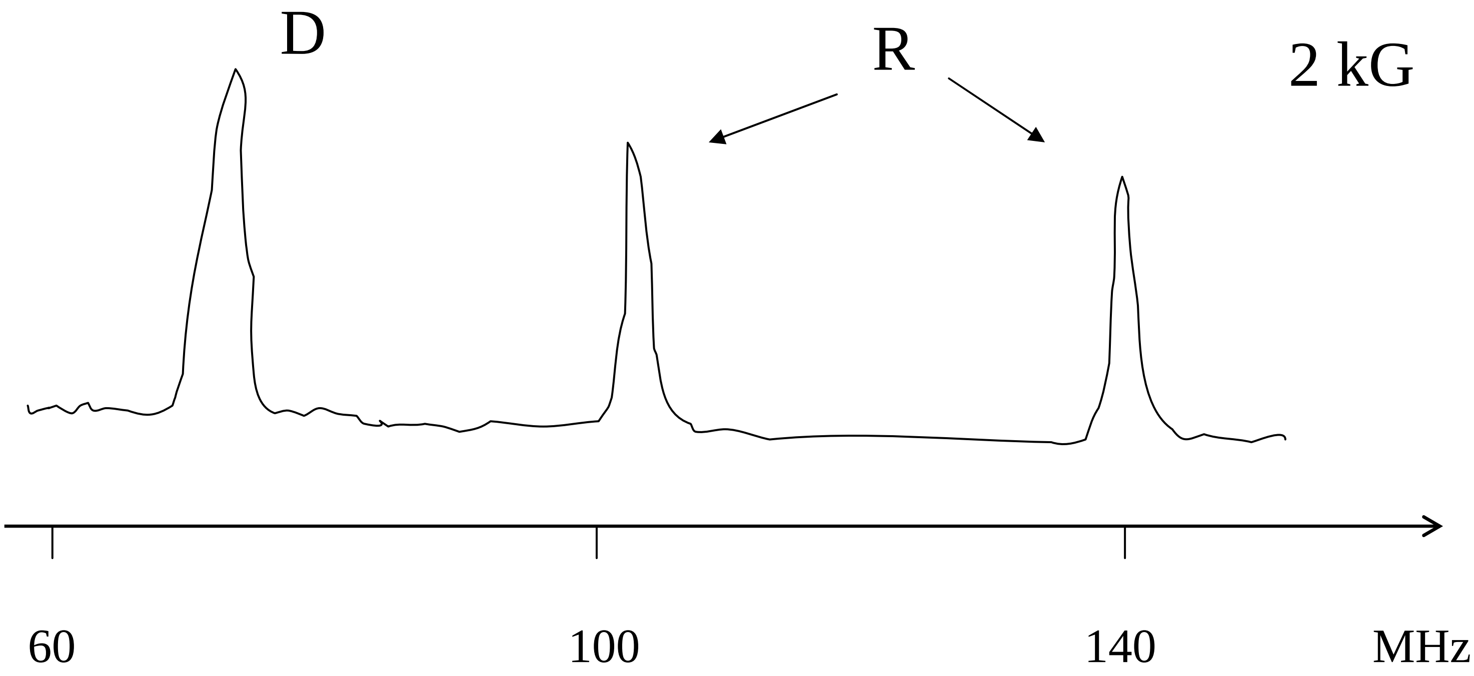
The spin hamiltonian describing this system is:

$$H_R = \omega_e S_z - \omega_\mu I_z^\mu + \omega_0^\mu S I^\mu - \sum \omega_k I_z^k + \sum \omega_0^k S I^k$$

In low magnetic fields the number of resonance lines will be observed, whereas in high magnetic field due to the decoupling all transitions degenerate to the two transitions only:

$$|\omega| = |\omega_\mu \pm ½ A_\mu|$$

Example: Fourier spectra of the muonated dimethylbutadiene radical(CH_2= •C_3H_3Mu) on SiO_2



D: muons in diamagnetic environment, R: muonated radical

Thus the linewidth, lineshape, resonance frequency, amplitude can be used in order to learn about the structure and dynamics of molecules adsorbed by surface of catalyst.

Formaldehyde $\mathbf{H_2C{=}O}$ is a good candidate in order to apply muSR for the investigation of rate constants of intermediates decomposition. Formaldehyde has unsaturated double bond similar to the acetone, where the muonated radical was observed (E. Roduner, P.W. Percival, D.G. Fleming, J.Hochmann and H. Fischer, Chem. Phys. Lett. 1978, 57, 37)

Expected reaction: H_3 C=O + Mu → H_3 C• –OMu (muonated radical)

Why it is important?

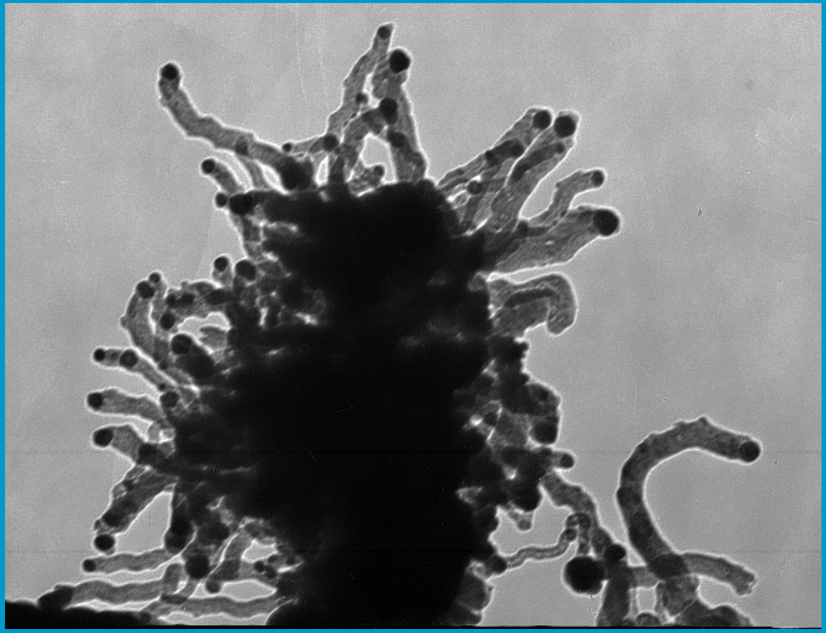
$$CH_3\text{-}OH \rightarrow CH_3\text{-}O \rightarrow H_2C{=}O \rightarrow C{=}O + H_2$$

Pt which is used as common catalyst is not efficient for decomposition of all intermediates. Development of new efficient types of catalysts.

Experiment

TF, temperature range: 243K-393K, magnetic field: 0.3kG<B<5kG
ALC, $\Delta M=1$ resonance ($B = A_{\mu}/\gamma_{\mu}$)

Catalysts: commercially available Pt on Vulcan XC-72; Pt-Ru alloys on Vulcan XC-72 and Carbon nanotube-Ni nanoparticles composites



Transmission electron microscopy image of carbon nanotube composite with Ni nanoparticles (dark spots)

Conclusion

Drink or feed the computer?