

Practical Fuel Cell

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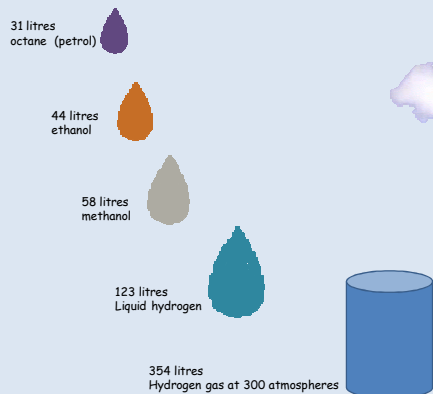


Figure 1. Volume and mass of fuel per 10^9 Joules

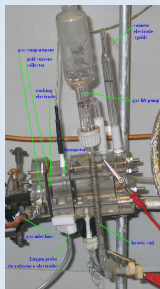
	litres / GJ	kg / GJ
H ₂ gas, 1 atm.	106142.3	8.70
H ₂ gas, 300 atm.	353.8	8.70
H ₂ liquid	122.9	8.70
methanol	57.9	45.85
ethanol	44.2	34.87
octane	30.9	21.62
lead acid cell	1376.7	121.40

Energy Source

Most modern technology needs a mobile form of energy. Sometimes we need to weigh up the exact cost of running our automobiles and domestic appliances, and soon we may be forced to do so by environmental legislation. The most complicated factor affecting these "footprints" is the choice of which energy reserve the machine wants to consume. Does it take grid electricity and thus have to consider losses in transmission, or consume hydrocarbons directly but at a lower conversion efficiency? Mobile machines cannot be attached to energy distribution networks, and so have to carry their fuel with them, and this limits us to a few media for storing energy.

Figure 1 represents the difficulty of carrying different energy sources in terms of the physical space needed to store the fuel, and in terms of the mass of fuel needed. Gibbs free energy of oxidation, ΔG° , is tabulated, since it is free energy that is accessed by cells (c.f. Enthalpy for combustion engines). In comparison with lead-acid and other metal batteries the energy stored in hydrocarbon fuel cells is particularly favourable since the table assumes that an air breathing cell can access atmospheric oxygen at no cost of carried mass, whereas metal cells use heavy cathodes such as lead oxide or MnO_2 .

Figure 3. Fuel cell test apparatus.



Nanoparticles – Platinum and Silver Coatings

With high innate catalytic action and stability, platinum is the metal chosen in practice for present fuel cells. The scarcity of platinum group metals has required the development of techniques for spreading it extremely thinly over the electrode.

Precipitation: Platinum salts are adsorbed onto carbon blacks, then reduced to metal in-situ.

Colloidal: Rapid reduction of platinum-ruthenium salts in solution produces small but imprecise crystals for later dispersion onto electrodes.

Micro-emulsion: Precise nanocrystals of 2.5 ± 0.2 nm can be produced by chemically reducing platinum salts dissolved in droplets of controlled size.

Alloying: Platinum-cobalt nanocrystals, optimally Pt_3Co , are more dilute in precious metal without loss of activity (surface cobalt dissolves).

Coating: Onto a compatible substrate such as WC. Eliminates waste of platinum within the non-utilised core of the crystals.

Silver is less active than platinum, but more abundant and with a falling industrial demand. We have chemically dispersed a coating of silver onto tungsten carbide nanoparticles, and demonstrated a 20% increase in the currents extracted from the fuel electrode over the base tungsten carbide, and improvement over the base silver which is less active than the carbide (Figure 6).

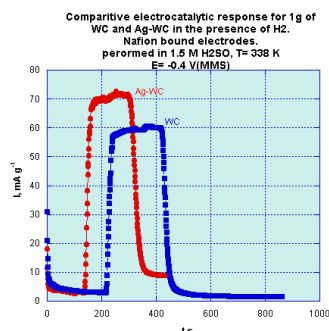


Figure 6.

Argon is flushed through the system initially, then hydrogen is switched on to replace it, producing a step increase in current. The size of the fuel current is confirmed when the fuel is switched back to Argon.

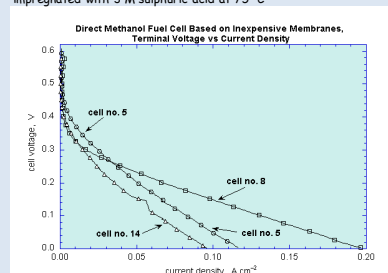
106 m³
Hydrogen gas, 1 atmosphere
(to the same scale as the other
fuels = entire area of poster)

A Low-Cost Membrane

We have investigated low-cost alternatives to the proton conducting polymer membranes used as the electrolyte in modern fuel cells. It is crucial to have a high electrical conductivity in the electrolyte layer that separates the electrodes. Therefore we have investigated using the most conductive mineral acid, sulphuric acid (at 3 M), infused into a porous support made from inexpensive and inert spun polymer.

Our most successful membrane was based on a porous polymer, and supported a current density over 200 mA/cm², in a direct methanol fuel cell with inputs of methanol vapour and air (Figure 4).

Figure 4. Direct methanol fuel cell performance, porous polymer impregnated with 3 M sulphuric acid at 75 °C



Electrocatalysts Based On Tungsten Carbide

A coating used for high friction machine parts, tungsten carbide is a surprising alternative for some catalytic processes that are otherwise unique to platinum. Synthesis can be from the oxide of tungsten, carburising at around 1000 °C under methane, or with solid carbon assisted with a liquid flux such as KCl.

We have demonstrated that tungsten carbide electrodes have a strong resistance to poisoning by carbon monoxide, losing only 2% of their activity when a fuel of pure hydrogen is mixed with 1% CO (Figure 5). This tolerance is lacking by pure platinum. Monoxide resistance makes tungsten carbide a good choice for air-breathing cells and for direct methanol fuel cells which generate carbon monoxide from their fuel. Its catalytic activity remains much less than platinum, however, and we are investigating novel synthesis techniques with the intention of improving this – such as shown in Figure 7.

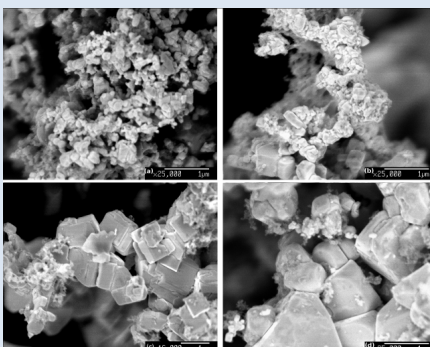
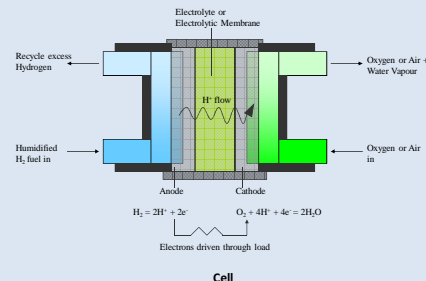


Figure 7. We have shown the synthesis of Tungsten Carbide to be strongly influenced by the presence of potassium chloride (5 weight %) and nickel (1 %). A basic synthesis from tungsten oxide and carbon (a) has its yield increased from 60% to 80% when the trace of KCl (b) is added as a liquid flux (molten above 771 °C), and up to 97% by the addition of nickel (d), which also accelerates grain growth. (Rees, 2007)

Aim:

To design inexpensive materials for use in mass-producible fuel cells.

Figure 2. Schematic of Fuel Cell



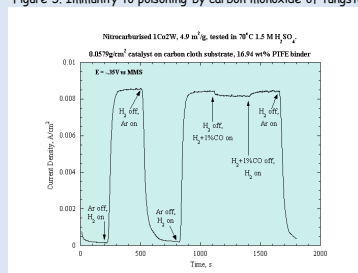
Cell

Electrical cells, modern versions of Alessandro Volta's 1800 zinc-silver cell, are among the few sources of portable energy. Replacing the reactive metal of a battery with a lighter reactive hydrocarbon is an obvious development that leads to extraction of electricity from a **fuel cell** (Grove, 1839). Fuel cells rated up to 12 kW have been used onboard the space shuttle since its first launch, and more recently twin 120 kW cells are found on the European type 212 submarine. Now the use of hydrogen fuel cells in space is popular since they extract more useful energy per unit mass of fuel than other methods such as combustion engines or metallic batteries. In other words they are a more fuel-efficient power source, and so of great interest in the current climate of high fuel prices and carbon emission charges.

Figure 2 shows a schematic for a typical low temperature fuel cell. Important reactions occur on both electrodes; frequently the rate of electrochemical reaction is the limiting factor for generating electrical power within the fuel cell. Optimising the catalyst layer is important, and several material systems have been examined. Some of these are summarised in the lower panels.

Our work has focused on non-platinum systems that will be more appropriate for large scale applications, on inexpensive electrolyte-bearing membranes, and on air-tolerant systems. We especially work towards materials suitable for vehicle fuel cells.

Figure 5. Immunity to poisoning by carbon monoxide of tungsten carbide



Embedded Nickel Systems

Alloys of nickel with more insoluble metals such as tantalum have been used in experimental fuel cells.

Nickel metal is a good catalyst; in alkali fuel cells using purified gas supplies, nickel is a possible electrode coating. But nickel dissolves in more robust acidic cells, so some strategy is needed to trap nickel within the solid catalyst layer on an electrode, while still having the nickel accessible enough to the material surface to have a useful activity. We have found nickel is stabilised when made in a glassy film with carbon and tantalum by sputter-deposition.

Sputtered electrodes are essentially flat, so their active surface area is far less than the highly porous materials that give large currents. A sputtered surface may have a specific area (true area per unit of coated surface) between 1 and 4, compared with 20 – 400+ for highly porous materials, and 1000+ for aerogels. The advantage of sputtering is that unusual compositions can be laid down. The modest currents that we have observed from this nickel-carbon system (with trace tantalum), in Figure 8, are somewhat promising if a high surface area material can be synthesised with the same activity per unit true area, and equivalent corrosion resistance.

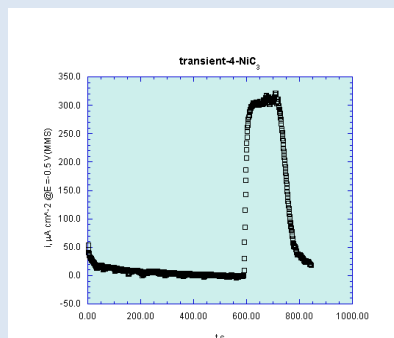


Figure 8. Hydrogen oxidation on sputtered nickel-carbon.

Low background currents indicate the nickel is passive in the catalyst. A 300 $\mu\text{A}/\text{cm}^2$ current from hydrogen oxidation is appreciable from a flat surface.

References

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