

[Slide Number 1 and 2]

Direct alcohol fuel cells, using alcohols as fuels, belong to proton-exchange membrane fuel cells (PEMFCs). In such systems, the fuel is oxidized directly at the surface of the electrode without reforming, which makes them attractive for portable power sources because the design of these systems is comparatively simple, the operating times are extensive, and the fuels can be easily produced from biomass. Direct alcohol fuel cells (DAFCs) are fuel cells that have high potential as an alternative for the production of distributed electrical energy and are particularly suitable for portable applications.

Direct alcohol fuel cells (DAFCs) have been increasingly attracting considerable attention as power sources for portable applications, arising from several unquestionable merits over analogous devices fed with hydrogen. Not only do alcohols, e.g., methanol, ethanol, glycerol represent considerably high volumetric energy density, but also their storage and transport are carried out much more easily compared with hydrogen. All these alcohols are readily available from natural gas, coal or biomass. Conversely, that the oxidation kinetics of alcohols are considerably slow has deteriorated their usage, and H₂-fueled polymer electrolyte fuel cells still present outstanding electrical performance in contrast with DAFCs possessing comparable electroactive surface areas. Hence, unceasing research attempts are being made to develop and design more effective anode electrocatalysts for DAFCs

Much DAFC research has focused on trying to elucidate the mechanism of the anode reaction. Like hydrogen and oxygen, the alcohols are adsorbed onto certain metals like platinum. Methanol is the smallest alcohol molecule and the easiest of all the alcohols to oxidize. In alcohols, there are three kinds of bonds: carbon bonded to hydrogen (CH bond), carbon bonded to carbon (CC bond), and carbon bonded to oxygen (CO bond). The Carbon and Hydrogen bond breaks most easily, the Carbon and Carbon bond is

more difficult to break, and the Carbon and Oxygen bonds do not break, even on a catalyst like platinum.

Methanol is considered to be the easiest alcohol to oxidize because there is no Carbon-to-Carbon bond to break. Accordingly, the DMFC has been studied the most. For a methanol fuel, there are only Carbon Hydrogen and Oxygen Hydrogen (from water) bonds to break and a Carbon oxygen bond to form.

[Slide Number 2]

In the past decades, there has been extensive research on direct methanol fuel cells (DMFCs) for portable power applications at low to moderate temperatures. Methanol is an attractive liquid fuel because it is relatively cheap, readily available, and easily stored and handled. Ideally, the electrochemical oxidation of methanol produces six electrons per methanol molecule. But, methanol has some disadvantages; for example, it is highly toxic, if not oxidized completely, is also toxic. In addition, methanol is not a primary fuel. These limitations have led researchers to investigate other alternative fuels.

However, direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC) are among the most notable DAFCs since they are widely studied and some prototypes and commercial products were produced. Advantages of using alcohols compared to hydrogen in PEMFC are due to their high energy density as well as easier storage, transport and refill. The most important step in designing a DAFC is the development of the anode oxidation catalyst. The electrochemical reactions in a DAFC produce carbon dioxide and water depending on the type of alcohol used. The electrochemical reactions in a DAFC are important as they will be critical and important for designing other components according to the type of DAFC.

[Slide Number 3]

Direct alcohol fuel cells (DAFCs) can generate electric power directly without converting liquid fuels into hydrogen as often occurs in proton-exchange membrane fuel cells (PEMFCs). Therefore, DAFCs work as simple as light power sources. Methanol is the most popular fuel of DAFCs. Ethanol is also used as a fuel in DAFCs, although its activity is much lower than that of methanol. The vapor pressure of these alcohols is so high that they are easily lost from fuel cells. Furthermore, high vapor pressure of methanol leads to its toxicity.

However, due to methanol leakage from the anode to the cathode, lowering cell voltage and thus power density and efficiency, the interest in DMFC for mass transport has reduced. Interest remains in specialty applications. The main market focus for DMFCs is in the areas of portable and micro-fuel cells. With the vast increase in high functionality portable consumer electronic devices (phones, laptops and entertainment devices) the need for increased battery power has driven micro-fuel cell development. Apart from specialty fuel cell companies (Polyfuel, Smart Fuel) all major electronic giants have programmes in the field and power densities of up to 1200 (three times the density of Li-batteries) have been reported. In the small portable sector they also show significant potential due to the simple fuelling infrastructure (methanol cartridges).

Recent announcements by leading developers claim significant progress with improved membranes and diffusion layers and clever fluidic designs. The mixed reactant approach with selective cathode and anode catalyst appears an interesting concept in this market segment. Despite the issues outlined above, DMFCs may become the first volume commercial products.

Production of alcohol can be achieved through the various processes and can play an important role in power generation. At the anode, alcohols split into hydrogen ions, carbon dioxide, and electrons. The electrons reach the cathode through an external circuit and the hydrogen ions which are positively charged diffuse from the anode to the cathode through a membrane known as polymer electrolyte membrane. At the cathode, hydrogen ions, oxygen, and the electrons react to produce water. The

temperature of less than 100°C is suitable for the operation of direct alcohol fuel cells and may be used as a power source in portable equipment like calculator, laptops, etc. The methanol fuel cell operates around $20 - 90^{\circ}\text{C}$. The reactions associated with the direct methanol fuel cell are given below.

Ethanol fuel is ethyl alcohol, the same type of alcohol found in alcoholic beverages, used as fuel. It is most often used as a motor fuel, mainly as a biofuel additive for gasoline. The development of ethanol as an aviation fuel was initiated because of a threat to the supply of aviation gasoline as a result of the Arab oil embargo in 1973. Ethanol is bad for cold-starting, because it doesn't burn as quickly as gasoline. (It has a higher octane, if you're interested.) Pure ethanol would be useless as fuel in the winter months. There are no passenger cars designed to take E100 (but some racing cars are) so it could damage your car engine.

[Slide Number 4]

Methanol has been considered as the best option for DAFCs mainly due to its relatively simple oxidation reaction mechanism when compared to other alcohols. However, methanol is toxic for human beings, highly volatile, and inflammable and is still considered nonrenewable. Furthermore, due to its relatively low molecular size, the methanol crossover is particularly significant in DMFCs that not only lowers the fuel utilization, but also degrades the cathode performance and generates extra heat, as will be explained later in the text.

Ethanol is an attractive fuel for direct fuel cells mainly because it is nontoxic and has a higher mass energy density than methanol. Moreover, ethanol is a potentially renewable fuel source, as it can be easily obtained from the fermentation of sugar-containing agricultural biomass [10]. Also, the carbon dioxide emitted from DEFCs can be recycled by planting, allowing a zero green-house contribution to the atmosphere. However, the cleavage of the Carbon-Carbon bond is very difficult making the ethanol oxidation rate

rather low. Platinum is the most active catalyst used, but self-inhibition occurs when used alone. Nevertheless, the DEFC performance is still poor, due to the incomplete oxidation of ethanol and needs to be improved. A major advantage of using ethanol is the lower crossover of the fuel through the membrane due to its higher molecule size.

[Slide Number 6]

DAFCs possess a wide spectrum of advantages as compared with proton-exchange membrane fuel cells (PEMFCs) that use hydrogen as the fuel. In addition, alcohol fuels are easily handled, transported, and stored. Unlike hydrogen-feed PEMFCs, liquid fuel-feed DAFCs do not need humidification and separate thermal management ancillary systems.

[Slide Number 7 and 8]

The DAFCs present the same general advantages of fuel cells, namely:

- potential for high efficiency;
- lower emissions when compared to conventional energy conversion technologies;
- simple design with no moving parts, promising low cost and high durability;
- modularity and, therefore, high scalability;
- no need of recharge, continuous power production as long as fuel is supplied to the cell

Some current limitations of fuel cells that also apply for DAFCs are:

- high cost due to the need of expensive materials such as platinum/ruthenium and other noble metals for the catalysts and Nafion;

- contaminants sensitivity—fuel cells require relatively pure fuel, free of specific contaminants;
- further improvements in power density (gravimetric and volumetric);
- fuel availability and eventual need of reforming, which increases the requirements of ancillary equipment;
- relatively low real durability due to start-stop cycling.

DAFCs present several advantages over their direct competitor hydrogen fuel cells. The main advantage is the use of a liquid fuel, which strongly simplifies handling and storage. In particular, for portable applications, mostly due to the lack of effective miniaturized hydrogen storage technologies, the use of a liquid fuel, requiring less ancillary equipment, is the best option to achieve a high power density with an attractive cost-to-power ratio. Small or micro-DAFCs can operate at room temperature reducing the thermal management challenges for small systems. The low operation temperature (typically $< 95^{\circ}\text{C}$) allows an easy start up and a rapid response to changes in load or operating conditions. However, the sluggish low temperature alcohol oxidation reaction prevents the DAFCs from obtaining similar levels of power density than hydrogen fuel cell. Another important disadvantage, already pointed out in the previous sections is the tendency of fuel crossover through the polymer electrolyte membrane.

Methanol also is a clean energy resource used to fuel cars, trucks, buses, ships, fuel cells, boilers and cook stoves.

Alcohol has been used to fuel cars since the dawn of the modern automobile. Henry Ford's Model T was equipped for running on ethanol as well as gasoline. And in recent years, the federal government has mandated that ethanol make up about 10 percent of most gasoline bought at the pump.

There are alcohol-driven engines, and you could use a vodka-fired Stirling engine easily enough, but you can't dump liquor into your gas tank without killing your car. (Though if it's rate for E85, you might be able to pull it off.) Alcohol is not a very good fuel, lacking a high energy density.

Formula 1 racing still uses gasoline, but NASCAR and Indycar use a mixture of ethanol and gasoline. The fuel used in NASCAR vehicles is mostly gasoline with a small amount of ethanol (E15), and the fuel used in Indycar racing is mostly ethanol with a small amount of gasoline (E85).

Among the other alcohols, ethanol is an attractive alternative to methanol as a fuel for fuel cells. Ethanol is a renewable fuel and can be produced in large quantities from farm products and biomass. Ethanol and its intermediates have been shown to be less toxic than other alcohols.

The key to current fuel cell catalyst research is based on the understanding that a fuel cell separates the electrochemical oxidation and reduction halves of the electrochemical combustion reaction. It is assumed that if the fuel or oxidation half-cell reaction and the oxygen reduction half-cell reaction can be made efficient, the fuel cell will very efficiently convert chemical energy to electrical energy, and flows of fuel to the anode and oxidant to the cathode will efficiently be converted into electric power.

The alloys of platinum and ruthenium (Pt—Ru), reported over 40 years ago, remain the best catalysts for methanol electrooxidation, as shown in reaction [1]. Yet, perhaps the greatest impediments to the commercialization of DMFC power sources are still the intrinsically low activity and high cost of the alloys of platinum and ruthenium (Pt—Ru) as well as the gradual loss of activity of Pt—Ru for catalyzing methanol oxidation.

[SLIDE NUMBER 9]

Direct alcohol fuel cells (DAFCs) are emerging technologies for the electrochemical conversion of the chemical energy of alcohol fuel, directly into electrical energy, with low environmental impact and high energy efficiency. However, before this technology can reach a large-scale diffusion, specific issues related to unsatisfactory electrochemical performance, high cost of cell components, and limited fuel cell durability must be solved. In a direct alcohol fuel cell system, high capital costs mainly derive from the use of noble metal catalysts, polymer electrolyte membranes, and expensive bipolar plates. Therefore, the development of cost-effective and high-performing polymer electrolyte membranes, enhanced electro-catalysts, and cheap bipolar plates, satisfying the target requirements of high performance and durability, represents an important challenge. The research is currently addressed to cost-effective materials, such as novel hydrocarbon membranes and low precious metal loading electrodes for applications in DAFC systems. These can find wide applications in portable, distributed, and remote electrical energy generation. Papers addressing components, systems, reaction mechanisms, cost analysis, cross-over, performance, and durability of direct alcohol fuel cells are solicited.