DIRECT ETHANOL FUEL CELLS: ETHANOL FOR OUR FUTURE FUEL CELLS?

RAPPORT 2015:137

BRÄNSLEBASERAD EL- OCH VÄRMEPRODUKTION

Energiforsk

Direct Ethanol Fuel Cells: Ethanol for our future fuel cells?

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ISBN 978-91-7673-137-6 | © 2015 ENERGIFORSK

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Förord

I syfte att koordinera teknikbevakning, samt sammanställa, analysera och sprida information om utvecklingen inom bränslecellsområdet till svenska intressenter, främst fordonsindustrin, finansierar Energimyndigheten ett projekt ”Teknikbevakning av bränslecellsområdet”. Projektet genomförs under 2014-2016 inom ramen för Svensk Hybridfordonscentrum (SHC) med Energiforsk som koordinator och projektledare.

Denna rapport är en förstudie som har tagits fram inom teknikbevakningsprojektet. Samtliga rapporter kommer att finnas publicerade och fritt nedladdningsbara på Energiforsks webbplats för bränslecellsbevakningen www.branslecell.se och på SHC:s webbplats www.hybridfordonscentrum.se.

Styrgruppen för projektet har bestått av följande ledamöter: Anders Hedebjörn Volvo Cars, Annika Ahlberg-Tidblad Scania, Azra Selimovic AB Volvo, Bengt Ridell Grontmij AB, Göran Lindbergh SHC/KTH, Elna Holmberg SHC och Bertil Wahlund Energiforsk AB. Energiforsk framför ett stort tack till styrgruppen för värdefulla insatser.

Stockholm maj 2015

Bertil Wahlund

Energiforsk AB

Sammanfattning

Bränsleceller baserade på etanol som bränsle är en möjlig framtida teknologi för fordonsapplikationer, främst på grund av bränslets fördelar, även om produktionssättet påverkar miljönyttan avsevärt. Etanol är världens mest använda bio-bränsle där infrastrukturen och logistiken redan finns tillgänglig inom stora delar av världen. Den mest attraktiva tekniska bränslecellslösningen för fordon är baserad på direct-etanolbränsleceller (DEFC) med alkaliska membran, AAEM, vilket möjligör användandet av Pt-fria katalysatorer. Även den höga verkningsgraden gör DEFC konceptet attraktivt, men avsaknaden av testade celler och prototyper för fordon gör att en viss skepsis inför konceptet existerar.

Syftet med denna förstudie är främsta att kritiskt identifiera potentialen för DEFCs och sammanställa ‘state of the art’ för teknologin ur ett fordonsperspektiv. Det finns flera frågeställningar som bör klargöras för att teknologin ska kunna skalas upp för fordonsapplikationer; frågeställningar som framförallt rör material, cell och systemlösningar för DEFC i sig självt, men även m a p bränsle och jämförande studier med konkurrerande teknologier. Utifrån denna förstudie har följande rekommendationer för fortsatta forsknings- och utvecklingsinsatser identifierats:

Primära:

Material och Celler
- AAEM-baserade koncept och utvecklingen av katalysatorer baserade på metalloxider.
- utröna temperatur och andra driftsparametrars påverkan på effekttäthet och komplexitet för celler för ett fordonssystem.

Fordon
- utvecklandet av modeller för fordonssimuleringar för att utvärdera olika systemdesignalternativ och resulterande fordonsprestanda.

Sekundära:

Bränsle
- känslighetsanalys av hur denatureringsämnen påverkar prestandan och livslängden för bränslecellen och bränslecellssystemet.
- utökade well-to-wheel (känslighets)studier för att utröna miljönyttan

Tekno-ekonomiska studier
- utvärdera potentialen för DEFC i fordonsapplikationer genom att benchmarka jämförbara elfordon baserade på: DEFC, DMFC och PEMFC, samt motsvarande batteridrivet fordon.

Summary

Fuel cells based on ethanol as fuel is one possible technology for vehicle applications, mainly due to the advantages of the fuel even if the fuel production highly affects the environmental benefits. Ethanol is the most used bio-fuel world-wide with an existing supply chain and infrastructure in many parts around the world. The most attractive direct ethanol fuel cell (DEFC) technology for vehicle applications is based on alkaline membranes, AAEM, enabling the usage of Pt-free catalysts. Also the high efficiency makes DEFC attractive, but the absence of cells and prototypes tested and evaluated in terms of vehicle demands makes the technology more challenging.

The aim of this study is to identify the potential of the DEFCs and to compile the state of the art for the technology from a vehicle perspective. There are several issues need to be addressed before the technology could be scaled up for vehicle applications; issues mainly related to materials, cells, and system solutions of the DEFC itself, but also related to the fuel and comparative studies of competing technologies. Based on this pre-study the following recommendations for future research and development activities have been identifies:

Primary:

Materials and cells

- AAEM-based concepts and development of metal-oxide catalysts.
- investigations how temperature and other operational parameters affects the power density and vehicle installation complexities.

Vehicle

- development of vehicle simulation models to evaluate system design constraints and corresponding vehicle performance.

Secondary:

Fuel

- sensitivity analysis of how the denaturalisation additives affect the overall performance and durability
- extended well-to-wheel analysis to determine the environmental impact.

Techno-economic studies

- potential of DEFC in vehicle applications: comparisons of EVs utilising different technologies: DEFC, DMFC, and PEMFC, in relationship to battery electric vehicles of same size and performance requirements.

Content

1 Introduction

Much of current research on fuel cell technology is based on the use of high quality hydrogen as fuel. This is in particular the case for low temperature fuel cells based on PEM technology (PEMFCs). PEMFCs have been one of the main routes towards environmental and sustainable solutions for the transport sector. From a genuine vehicle perspective, however, a liquid fuel is of prime interest due to the simplicity in usage, handling and integration. Therefore, efforts on reforming liquid fuels like diesel to hydrogen gas have been plentiful. Another path has also been in focus – the use of methanol as a fuel in direct methanol fuel cells (DMFC).

For the latter considerable R&D has found limitations both concerning the basic technology requiring development of new materials and the need for development of infrastructure to distribute methanol at a larger scale. The DMFC has several disadvantages compared to the PEMFC, like the slow kinetics of the methanol oxidation, methanol crossover, and anode poisoning by strongly adsorbed intermediates (mainly CO) [1]. A reduced efficiency due to the methanol crossover has been reported [2], and will also reduce the potential of the cathode and lead to a waste of fuel [3]. Moreover, methanol is a toxic and flammable fuel.

To overcome the issues with methanol, ethanol is at a first instance a very attractive substitute since it has the advantage of being non-toxic and has a higher energy density (8 *vs.* 6 kWh/kg). Another advantage is the existence of a supply chain; delivery of fuel is not a concern. Ethanol is already available on an industrial scale from a variety of sources and has many applications as a liquid fuel *e.g.* E85. There are, however, issues originating from well-to-wheel analyses where the production largely determines the overall sustainability of ethanol as a fuel – and thus also for any fuel cells driven by ethanol. For a broader perspective on various ways to create a future fossil-free transportation system in Sweden, including these issues, see [4].

The scope of this study is to critically identify the potential of the direct ethanol fuel cells (DEFC) technology and to compile the present state of the art with due input from a vehicle perspective including any active actors as well as comparisons with the PEMFC and DMFCs concepts. Indeed, DEFCs ideally work very much like DMFCs, but has shown to exhibit a lower crossover rate affecting the cathode performance less severely [5]. The DEFC technology is currently under (rapid) development and today most of the cells existing are at lab scale running <100 h, but the technology has a promise of an efficiency of about 80% and the energy price can be as low as $0.04/kWh [6]. However, being a rather new technology there are several issues that still need to be addressed on several different levels, primarily the basic technical requirements, cell solutions, and the integration in vehicles. Secondary, also the fuel production and distribution should be addressed, where we cannot exclude to note the advantage of an existing distribution network and refuelling infrastructure. Finally, research opportunities for various levels of Swedish stake-holders are to be recommended.

2 Basic Principles and Concepts of DEFCs

In a DEFC ethanol is electrocatalytically converted directly at the anode to protons, CO_2 and water. There are two basic types of DEFC concepts: PEM-based and AEM-based (AEM = anion-exchange membrane). The main challenge for the PEM-based concept is the slow kinetics of the ethanol oxidation at the anode. Utilising both acidic media and Pt catalysts have not been successful to overcome this kinetic issue. An AEM-based concept shows faster kinetics for both the ethanol oxidation and the oxygen reduction reaction (ORR) than the PEM-based concept, and higher efficiencies have been shown [7-10].

The specific energy of ethanol is 8.03 kWh/kg, compared to 32.8 for hydrogen. Taking the density of the fuel into account, however, the energy density of ethanol is 6.28 kWh/L (0.18 kWh/L[1] for compressed hydrogen). The DEFC theoretical energy efficiency under reversible conditions, defined as the ratio between the electrical energy produced and the heat of combustion at constant pressure, is 97%. Under working conditions, however, the cell voltage, severely affected by the current density, is much lower and thereby also the practical efficiency attainable for the DEFC. More realistically, working at 0.5 V and 100 mA/cm^2 with complete oxidation of ethanol to CO_2, result in an efficiency of 40%, and hence the DEFC is in the same range as a diesel ICE.

There is not only one type of DEFC possible for vehicle application; below the most promising variants are described primarily based on the very details of the technology upon which the cells are based – cell reactions *etc*.

2.1.1 PEM-based DEFC

In the PEM-based DEFC concept, ethanol is fed into the anode in a diluted state and consumed/converted according to the following reaction:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$$

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[1] H_2 storage at 70 bar and 25 ºC.

The involvement of twelve electrons is attractive from a performance perspective, since the standard potential, E°, of the cell is affected by the number of electrons, n, according to the Nernst Equation:

$$E^0 = -\frac{\Delta G^0}{nF}$$

At the cathode oxygen is reduced according to the following reaction:

$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$$

The overall reaction of the DEFC is thus:

$$C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$$

It should be noted that CO_2 thus is produced in a DEFC, just like in a DMFC, but unlike a PEMFC running on hydrogen. One challenge utilising PEM-based DEFC concepts is the ethanol crossover, in the same manner as for DMFC. The ethanol crossover will be further discussed below (4.1.1).

2.1.2 AEM-based DEFC

This concept has many similarities with the alkaline FC (AFC) utilising an anion-exchange membrane (AEM). Using alkaline media the DEFC exhibits lower polarisation for the oxidation of ethanol than in acidic media, with the same platinum catalyst. Furthermore, the AEM concept also allows for the possibility to use non-platinum, less expensive, metal catalysts. Also, the ethanol permeation rate is reduced by the reversing of direction of ionic current, due to hydroxide ion conduction, compared to the PEM concept [11-13].

The AEM-based DEFC has the exact same overall cell reaction as the PEM-based. The difference is that the ethanol is diluted in an alkaline solution instead of water, and the corresponding anode and cathode reactions, respectively, are:

Anode: $C_2H_5OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^-$
Cathode: $3O_2 + 6H_2O + 12e^- \rightarrow 12OH^-$

Usually, NaOH or KOH is the source for the hydroxide ions. Through the membrane the hydroxide ions are transported from the cathode to the anode. Consequently, there is no electro-osmotic flow of ethanol and the only contributions to the ethanol crossover are diffusion and hydraulic permeation due to concentration and pressure gradients, respectively. Some of the attractive characteristics for the AEM-based concept are the less corrosive environment, enabling longer durability than in the acidic PEM-based concept, and the faster kinetics of the ORR, allowing the use of Pt-free catalysts.

2.1.3 AAEM-based DEFC

To even further improve the performance of a DEFC, especially to increase the performance of the anode catalysts at lower temperatures and anode surface poisoning by CO-like intermediates [14], there is a DEFC concept combining alkaline and acidic media in a single cell: the alkaline-acid DEFC – AAEM-DEFC [7,12]. The anode is in alkaline media and the cathode is in acid media by using a PEM-type membrane (due to the favourable thermal stability and ionic conductivity compared to an AEM-type membrane).

3 Important DEFC Phenomena

3.1.1 Ethanol crossover

As should be clear from above, a very significant challenge in developing membranes (PEM, AEM) for the DEFC is to avoid ethanol crossover through the membrane, *i.e.* that ethanol is transported, together with protons, through the membrane from the anode to the cathode without taking part in the electrochemical reactions. This creates a mix-potential and reduces the efficiency and the overall cell performance.

The rate of ethanol crossover decreases the current through the DEFC, and the efficiency of the DEFC can be described according to:

$$\eta = \frac{i}{i + i_x}$$

where i is the current density of the DEFC, and i_x is the crossover current, *i.e.* the current which is not generated because of the ethanol crossover. In a DEFC, however, it is yet not clear if the reduced current density is due to ethanol crossover or incomplete oxidation, or to both. By measuring the ethanol concentration in the anode exhaust and the concentration of both ethanol and CO_2 at the cathode outlet, this can possibly be quantified. Ethanol in a DEFC has lower crossover rates and affects the cathode performance less severely than the methanol in a

DMFC. This is due to a lower permeability through the membrane and slower oxidation kinetics [1,15]. The ethanol and its oxidation intermediate products, however, both have the potential to poison the catalyst of the cathode [16].

Generally, the ethanol crossover rate will increase with temperature, current density, and anode inlet concentration [17,18]. High concentrations (> 4M) can result in volcanic behaviour [19,20]; a behaviour related to the solubility of ethanol and the swelling of the membrane [19] affecting both the total crossover rate, diffusion, and electro-osmotic drag.

There are ways to minimize the crossover, and one route is to use composite membranes consisting of a polymer (*e.g.* sulfonated polyether-etherketone, SPEEK) and inorganic components (silica nanoparticles) [21]. This can act as a barrier against ethanol loss while maintaining proton conductivity in the case of PEM fuel cells. Subsequent cross-linking of the silica particles further enhances membrane stability.

3.1.2 Oxidation of ethanol

The second specific problem of DEFCs is to optimize the oxidation of ethanol at the anode. The oxidation reactions of ethanol differ depending on the electrolyte characteristics, *i.e.* if an acid or alkaline media is used. The reaction involves multistep mechanisms with adsorbed reaction intermediates and the possible formation of by-products, which may diminish the efficiency and may result in unwanted products unable to further oxidise [22,23].

The reaction mechanisms occurring in *acidic media* have been investigated by several techniques and research groups, *e.g.* [23-27]. In order to achieve a high efficiency the C-C and C-H bonds in ethanol need to be cleaved, otherwise the following reactions can take place:

$$C_2H_5OH \rightarrow CH_3CHO + 2H^+ + 2e^-$$

(*i.e.* formation of acetaldehyde)

$$C_2H_5OH + H_2O \rightarrow CH_3CH(OH)_2 + 2H^+ + 2e^-$$

$$C_2H_5OH + H_2O \rightarrow CH_3CHOOH + 4H^+ + 4e^-$$

(*i.e.* formation of acetic acid)

The formation of these intermediate products results in a significant decrease of the energy content. As a first step in the oxidation reaction ethanol is adsorbed and oxidised on Pt by forming Pt–OCH_2CH_3 and Pt–$CHOHCH_3$ [28,29]. Thereafter, these species are transformed to Pt–$COCH_3$ and Pt–CO, which in turn can be further oxidised to CH_3COOH or preferably CO_2. For the latter reactions, adsorbed OH species play an important role [28,30,31]. Acetic acid is a dead end, *i.e.* no further oxidation is possible [32].

The complete oxidation of ethanol is dependent on parameters like ethanol concentration, temperature, potential, and the catalyst used. From studies of DEFCs running at room-temperature and using polycrystalline Pt catalysts it has been concluded that the concentration of ethanol influences the reaction paths and the extent of which the acetaldehyde or acetic acid is formed [33]. Other studies have concluded that the catalyst loading plays an important role in order to efficiently cleave the C-C bond [34]. At higher temperatures, at about 250 °C, a high degree of C-C cleavage (about 90%) can be obtained utilising a Pt/C catalyst and a solid proton conducting membrane of CsH_2PO_4 almost independent on the potential applied [26].

On the other hand, in *alkaline media* the kinetics of the ethanol oxidation are faster than in acidic media. One reason is the increased adsorption of OH, which can further increase the formation of CO_2 [30,31]. The challenge to fully oxidise ethanol is still to avoid the formation of acetaldehyde and acetic acid [35]; as in the acidic media, acetaldehyde is able to be further oxidised, but acetic acid is not [36,37].

The temperature is the most important operational parameter affecting the CO_2 yield in alkaline media [35]. It has been discussed how the potential affects the CO_2 yield, as CO_2 is mainly generated from adsorbed CO species, formed at low potentials and that bulk oxidation is not possible [35,38]. Moreover, the effect of the ethanol concentration has been investigated. The highest efficiencies were obtained at 1M NaOH and CO_2 were only detected at pH below 13, stressing the importance of having a large amount of adsorbed OH to achieve high oxidation activity [39].

The usage of Pt-catalysts is not optimal due to their sensitivity to CO poisoning and a corresponding decrease in cell performance. High performance is achievable, but not optimal in terms of CO_2 yield. Pt-based bi- or tri-metallic catalysts are therefore used to enhance the ethanol oxidation. The catalysts used are often on carbon support, *e.g.*

Pt/C, Pt-Sn/C, Pt-Ru/C, Pt-Pd/C, PtRuSn/C, where Pt-Sn/C is one of the most active catalysts [40]. The CO_2 sensitivity is lower when utilising Ru than Sn at higher potentials, and an increased Ru content results in increased catalytic activity, but with a reduced capability to cleave the C-C bond [41]. Sn is more efficient in increasing the performance and having the capability to prevent from CO poisoning. Moreover, Re is able to efficiently cleave the C-C bond when combined with other ethanol oxidation catalysts [42]. Introducing Rh in the Pt/C catalyst has been shown to improve the C-C cleavage in alkaline media, but not in acidic media [43].

The Pd-based catalysts seem to be superior for ethanol oxidation, especially in alkaline media [44]. The activity if Pd/C promoted with nanocrystalline oxide catalysts (*e.g.* CeO_2, Co_3O_4, Mn_3O_4, and Ni-oxides) in alkaline media [45], and these catalysts achieved higher efficiencies and were less sensitive towards CO poisoning. A group of catalysts based on nanostructured Fe-Co-Ni alloys have been proven to be efficient in alkaline media with power densities of 30-40 mW/cm^2 at room temperatures and about 60 mW/cm^2 at 80 °C [46]. Challenges are still the durability due to the formation of metal oxides on the surface of the catalysts [47]. One route to improve the durability is to coat non-noble catalysts with a thin layer of Pd [48]. An example of ethanol oxidation catalyst for alkaline media is utilising a three-dimensional Ni-foam coated with Pd. The benefits are the lack of electronic conductivity, low weight, and high surface area, and would reduce the diffusion resistance enhancing the ion transport [49].

4 Ethanol as Fuel

To enable a fair assessment of the DEFC technology compared to its competitors, both the basics of the technology itself, the pre-requisites for vehicle implementation, but also the fuel to be feed must be reviewed briefly. Ethanol is a serious candidate as alternative fuel for the vehicle industry, with a market penetration and established logistics of production and distribution, independent of any FC technology. Due to high energy density (70% of gasoline), being liquid and low toxic, ethanol can give fuel cells a mass-market appeal. The main drawback is the questionable environmental impact at a global scale. In Sweden half of the yearly consumption is domestically produced. The worldwide production was 23 429 million gallons in 2013 [50], >80% of all bio-fuels produced, and projected by the International Energy Agency (IEA) to grow further [51].

Another drawback of ethanol as a DEFC fuel is the legal requirement of denaturalisation. In Sweden, all liquids with ethanol contents higher than 70% must be denaturalised with 0.25 % methyl-4-butyl-ether (or ethyl-4-butyl-ether) and 0.5 % iso-butanol. Moreover, the fuel must be red-coloured [52]. Virtually all DEFC tests have been made without taking these issues into account – which might be a show-stopper for the technical implementation.

In Table 1 below the main properties of various FC fuels are compared.

Table 1. Hydrogen, methanol, and ethanol as FC fuels for vehicles.

	H_2 (700 bar)	Methanol	Ethanol
Theoretical specific energy (kWh/kg)	32.8	6.07	8.03
Electrical energy density (kWh/L)*	1.3	4.3	6.4
Boiling point (ºC)	N/A	67.4	78.0
Vapour pressure @ 20 ºC (mbar)	N/A	129	58
Availability & Infrastructure	No	No	Yes
Simplicity of handling	--	+	+***
Toxic	No	Yes	No
Explosive	Yes**	No	No
Flammable	Yes	Yes	Yes

*[53], **related to tank, *** “-“ if diluted alkaline solution of ethanol is considered

5 State-of-the-art

There are several studies on the performance of DEFCs with a variety of operational constraints: base concepts, temperatures, ethanol concentrations and diluent, current densities, catalysts used, *etc.* The state-of-the-art for DEFC cells is summarised in Table 2 below. The performance measure is mainly the power density at optimal conditions and given at the FC level, i.e. not at the installation level. For internal comparisons across different DEFC technologies there are few or no differences in installation when aiming at the same application (here vehicles). A seldom mentioned complication of the AEM or AAEM concepts is that the fuel is a diluted alkaline solution of ethanol (see Table 1). Hence, in a vehicle installation this is a severe complication to the ease of handling the liquid fuel – often seen as one prime advantage of DEFC compared to hydrogen based PEMFCs. For DEFCs based on PEM technology the corresponding problem remains, but the then need for an aqueous solution is similar to the needs of a DMFC.

Table 2. State-of-the-art of the DEFC technology utilising oxygen as the cathode.

Type	Anode catalyst	Temp. (°C)	Power density (mW/cm^2)	Ref.
AEM	PtRu	90	61	[54]
AEM	Pt/C	75	49	[11]
AEM	Pd-(Ni-Zn)/C	20	58	[11]
AEM	RuV/C	80	90(air)/110(O_2)	[11]
AAEM	PtRu/C	20	58	[37]
AAEM	PdNi/C	60	240	[14]
AAEM	PdNi/C	60	360	[55]

All these examples above are for lab sized cells at a sub-vehicle need scale. There are today no examples in the open literature of DEFCs sized for vehicle needs*, and also no commercial actors easily identifiable working to reach these sizes, which points to a very low maturity of the field. All major activities discernible are occurring at universities and research institutes. Based on the state-of-the-art the R&D efforts on DEFCs should hence still be directed both towards fundamentals – finding the best materials and concepts including the possibilities to up-scale small lab cells, and subsequent feasibility studies in terms of real working DEFC at the sizes adequate for vehicles. This is thus in stark contrast to foremost hydrogen based PEMFCs, and partially also compared to DMFCs – but also the latter has not yet been properly sized for vehicle needs.

In order to compare different FC technologies, overall ranges of typical performance characteristics for DEFCs, DMFCs, and PEMFCs are given in Table 3. The present state-of-the-art for the DEFC technology does not allow any proper size, weight, or cost analysis at the vehicle level (see above). There is, however, no reason to assume any other peripherals needed for a DEFC vehicle installation as compared to the installation of a DMFC – hence these two technologies should be approximately the same in all important aspects.

Table 3. Ranges of performance characteristics for the DEFC, DMFC, and PEMFC technologies, and approximate costs [56].

Technology	Cell Op. temp. (°C)	Cell fuel efficiency	Cell power density (mW/cm^2)	Cell cost ($/kW)
DEFC	20-90	30-60	10-400	1000?
DMFC	25-150	30-45	50-200	1000
PEMFC	25-100	40-50	500-1000	50-2000

* There are examples of a DEFC being used to power vehicles – the first being designed by students from Offenburg, Germany, for the Shell Eco-marathon in 2007 [57]. We do not think such an application warrants any special consideration as state-of-the-art in light of the very odd requirements and vehicle target.

6 SWOT analysis

In order to get a better understanding of the possibilities and limitations of the DEFC technology for vehicle applications, based on the state-of-the-art above, a comprehensive SWOT analysis have been made. In the following sections the strengths, weaknesses, opportunities, and threats are given including explanatory sections to each of the factors listed and the level of uncertainty where appropriate. All the properties identified are reviewed in the light of comparing the DEFC technology vs. both other FC technologies (DMFC and PEMFC), but also *vs.* battery technologies suitable for vehicle application.

6.1.1 Strengths

The following strengths have been identified:

- High fuel and energy efficiencies
- Liquid and low-toxic fuel
- Existing fuel infrastructure

As seen above the strengths of the DEFC are primarily connected to high efficiencies and to ethanol as fuel. The high efficiency refers to both to theoretical and practical energy efficiencies – the latter only proven, however, for sub-vehicle sized FCs. Depending on the realization of the promises of the state-of-the-art also power density could be a strength – but is yet to be proven, even if the reduced crossover current should result in higher voltages and more power of DEFCs than for DMFCs. The other strengths are related to the fuel being liquid (easy to store, transport, and handle) with important inherent advantages for vehicle installation and safety. The existing infrastructure is an added strength to the overall concept

6.1.2 Weaknesses

The following weaknesses have been identified:

- CO_2 emissions
- C-C catalyst needed
- DEFC reactions not complete
- Low ethanol concentration in practice
- Only denaturalised ethanol legal
- Mostly micro-scale cells developed – no vehicle demonstrated
- Well-to-wheel analysis results

From an environmental perspective a major weakness is the inherent production of CO_2, but also that higher alcohols are likely to be formed – lowering the energy efficiency – incomplete reactions. Compared to both hydrogen PEMFC and DMFC, DEFC suffer from the need of catalysts capable, with high efficiency, to cleave the C-C bond in ethanol – which in the end can be a show-stopper for the technology. As a consequence, often the anode inlet mixture has a lower ethanol concentration than stoichiometry, which will lower the efficiency on vehicle level due to the need of larger fuel tanks *etc*. For an AEM based DEFC the construction of a tank of ethanol diluted in alkaline solution is a major weakness at the vehicle installation level.

The major weakness for the DEFC as of today, however, is that no cells of any size close to those of interest to power vehicles (stacks/systems) have been demonstrated – and thus most performance is based on uncertain up-scaling of micro- to mini-DEFC cell data or by comparisons with DMFCs. Indeed, most DEFCs are truly micro-FCs. There are also no commercial actors identifiable, why the technology must be judged as quite immature. This is of course then also true when it comes to size, weight and cost estimates for vehicle installations. Here also the current rapid development of battery powered electric vehicles come into play – if the DEFC installation becomes surpassed in terms of both driving range and installation requirements – the technology will not be commercially competitive.

Another weakness is that in Sweden, by law, all ethanol for vehicles must be denaturalised – which might reduce both the (catalyst) efficiency and the life-length of any DEFC. If a cleaning stage is needed on-board the vehicle – the installation becomes severely more complex, likely somewhere between on-board gas-purification and diesel reformation. To this fact we also add the uncertainty of whether or not then a well-to-wheel analysis would produce results in favour of the DEFC technology.

6.1.3 Opportunities

The following opportunities have been identified:
- Lab demonstrator of larger DEFCs
- Catalyst development
- Domestic fuel production and industry

Even if the system described in [57] cannot be seen as a “real” vehicle implementation of a DEFC in general, the conclusions gained from the study provide opportunities for further development of the DEFC technology for vehicles by creation of larger scaled cells. Vehicle sized DEFCs are thus deemed possible, but the both the largest needs and opportunities for the technology are related to the development of low-cost catalysts having high ethanol oxidation yields. One possibility of the catalyst selection is that AEM-based DEFCs has advantages over PEM-based due to use of Pt-free catalysts for the cathode, which would reduce the cost as well as increase the efficiency. Like many FCs, the major downside to DEFCs is the cost related to catalysts and the risk of catalyst poisoning by carbon monoxide. There has been less research invested into DEFC catalysts, so they tend to be behind the curve in terms of technology.

6.1.4 Threats

The following threats have been identified:

- Up-scaling issues for the DEFC
- Battery (r)evolution
- H_2 infrastructure build-up
- Political issues of fuel *vs.* food

As for all new technologies, threats can be easily identified, but at the same time these treats can be overcome by scientific and technological actions. One of the main treats for any FC technology for vehicle applications comes from the battery development, making vehicles utilising batteries more attractive in terms of cost and driving range. On the other hand, maybe the main threat for battery electric vehicles is indeed the development of competitive FC solutions, with PEMFC being the current champion. The lack of widespread hydrogen refuelling infrastructure is, however, not in place, unlike for ethanol, while the latter fuel has a political disadvantage globally with doubts on large-scale production leaving reduced land for farming for nutritional needs and hence jeopardizing the food chain.

The major threat, however, is that there currently are no sizeable DEFC despite some efforts – and up-scaling might be intrinsically very difficult, and that the lead other FC technologies have will mean that the needed large efforts for this development for DEFCs never will be realized.

7 Conclusions and Recommendations

The DEFC technology would be an attractive solution for vehicle application mainly due not to the cell itself, but to the fuel: the widespread ethanol production, supply chain, infrastructure, and usage as bio-fuel worldwide – even if not without complications.
The DEFC technology could in the end be a cost-effective solution for vehicle applications due to high efficiency and the possibilities to utilise Pt-free catalysts for the cathode reactions in alkaline media – with the most attractive solution being DEFCs based on AAEM membranes.
The lack of sizeable cells and commercial actors make it virtually impossible to apply the state-of-the-art of DEFCs to vehicle application without large uncertainties. This is also true for the needed up-scaling of the technology.

Based on this minor pre-study, the following recommendations are given for research and development opportunities.

Primary:
Materials and Cells
As for all fuel cell technologies and concepts the material properties are the key for performance, cost, and durability. The performance of the AAEM-based concept needs to be further understood and the usage of metal-oxides as catalysts would be possible to further improve. In Sweden we do have a knowledge base for research and development in this area due to the long experience within the field of PEMFCs: polymers, catalysts, MEA, electrochemistry, system design, both in academia and in industry (for example my-fc, PowerCell, and Cellkraft). Furthermore, the temperature performance and the constraints on materials used need to be understood for power density and vehicle installation complexities. When all materials are in place prototype cells of sizes attractive for vehicles should be developed – not unfeasible in the light of the large FC experience in Sweden.

Vehicle performance
Based on literature and test data, vehicle simulation models should be set-up in order to evaluate the system design constraints and the corresponding vehicle performance. Such studies should also consider the balance of plant components needed, for example if a power-supporting system is required (*i.e.* are batteries or super capacitors needed for acceleration performance). Based on vehicle simulation

studies the most optimal operating parameters and durability can be achieved.

Secondary:

Fuel

The fuel as such is rather uncomplicated to a fuel cell system in a vehicle, but the major concern for DEFCs is related to both the denaturalisation additives needed according to law and to the diluted fuel used in practice in the cell. For the former standards and regulations have to be reviewed from an international perspective. Sensitivity analysis of fuel purity and how these additives affect the fuel cell performance, mainly the catalysts, needs to be understood and if a cleaning device must be included. Moreover, additives may differ depending on geographic region and therefore must be considered in such a sensitivity analysis. Compatibility of ethanol and fuel additives with other components in DEFC system is also a key for vehicle applications. For the latter point, the implications on vehicle installation must be accounted for – also in the efficiency evaluation compared to competing technologies – unless materials development (above) allows the use of concentrated ethanol as fuel.

Techno-economic studies

In order to understand the potential of DEFC in vehicle applications techno-economical studies needs to be performed by comparing EVs utilising different fuel cell technologies: DEFC, DMFC, and PEMFC. Such studies should take the full vehicle into considerations, *i.e.* fuel tank and balance of plant components. Moreover, the CO_2 emissions should be considered for the direct alcohol based technologies. Battery electric vehicles of the same size and performance requirements should also be used for comparison.

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DIRECT ETHANOL FUEL CELLS: ETHANOL FOR OUR FUTURE FUEL CELLS?

Bränsleceller baserade på etanol som bränsle är en möjlig framtida teknologi för fordonsapplikationer. Den mest attraktiva tekniska bränslecellslösningen för fordon är baserad på direkt-etanolbränsleceller (DEFC) med alkaliska membran, AAEM, vilket möjliggör användandet av Platina-fria katalysatorer. Även den potentiellt höga verkningsgraden gör DEFC-konceptet attraktivt, men avsaknaden av testade celler och prototyper för fordon gör att en viss skepsis inför konceptet existerar.

Syftet med denna förstudie är främsta att kritiskt identifiera potentialen för DEFC:s och sammanställa 'state of the art' för teknologin ur ett fordonsperspektiv. Det finns flera frågeställningar som bör klargöras för att teknologin ska kunna skalas upp för fordonsapplikationer; frågeställningar som framförallt rör material, cell och systemlösningar för DEFC i sig självt, men även med avseende på bränsle och jämförande studier med konkurrerande teknologier.

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Energiforsk är en forsknings- och kunskapsorganisation som samlar stora delar av svensk forskning och utveckling om energi. Målet är att öka effektivitet och nyttiggörande av resultat inför framtida utmaningar inom energiområdet. Vi verkar inom ett antal forskningsområden, och tar fram kunskap om resurseffektiv energi i ett helhetsperspektiv – från källan, via omvandling och överföring till användning av energin. www.energiforsk.se

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