Direct Converting Low Temperature Bio-Ethanol Fuel Cells

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1 Introduction

Bio-ethanol is a renewable fuel with low CO_2 emissions. However, as its production conflicts with the production of food, it will not become abundantly available. A sustainable use therefore requires high efficiency. Fuel cells can deliver the required efficiency in producing electricity from bio-ethanol, in particular when direct conversion is possible. In low temperature fuel cells, which are suitable for a number of applications, conversion of ethanol is often hindered, leading to an incomplete oxidation of the fuel. As this incomplete oxidation reduces the conversion efficiency and can result in the formation of undesired by-products such as acetaldehyde, it should be avoided. Optimisation of the catalyst and the electrode layers is therefore required in order to use ethanol in low temperature direct ethanol fuel cells. This optimisation needs to be carried out separately for all fuel cell technologies of interest. Currently available fuel cell technologies of interest are low-temperature proton exchange membrane fuel cells LT-PEMFC, alkaline anion exchange membrane fuel cells AEMFC and high-temperature proton exchange membrane fuel cells HT-PEMFC. Within this project, the electrochemical behaviour of ethanol at platinum electrodes at ambient temperature was investigated in both acidic and alkaline environments, employing standard electrochemical techniques such as cyclic voltammetry (CV), chronoamperometry (CA) and differential electrochemical mass spectrometry (DEMS). Additional tests were carried out for the oxidation of acetaldehyde as a known intermediate. Furthermore development of LT-PEMFC electrodes and membrane electrode assemblies was performed, allowing for the stable operation of a DEFC at ambient temperature with passive air supply. Additional tests on AEM-DEFC showed the high potential of this technology.

2 Electrochemical Behaviour of Ethanol

Electrochemical reactions are often hampered by adsorbates formed from the substrate which bind too strongly to the surface to be easily removed. In the case of the ethanol oxidation reaction, in order to find such adsorbates and determine their nature, stripping measurements were performed in a flow-through DEMS cell. For these measurements the electrode surface was cleaned by repeatedly cycling the potential of the electrode in neat electrolyte solution between the hydrogen and oxygen evolution potential until a stable base CV was observed. Subsequently the electrode potential is set to the desired adsorption potential and ethanol in electrolyte solution is admitted to the cell during the adsorption period. Finally the electrolyte is replaced by neat electrolyte again, and after all ethanol

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signals have disappeared from the MS the electrode potential is cycled starting either in the anodic or the cathodic direction. In the case of the stripping of ethanol adsorbed from acidic solution, a number of studies can be found in literature[1-3]. In this project the results were compared to those for ethanol adsorption from alkaline solution. Comparable behaviour was observed. Adsorbing ethanol onto a cleaned polycrystalline platinum surface leads to the formation of two types of adsorbates differing in their desorption potentials during the anodic sweep of the stripping cycle. As can be seen from Figure 1 two oxidation peaks at about 0.6 V vs. RHE and 1.1 V vs. RHE, respectively are observed during the stripping of ethanol adsorbates, both giving CO_2 as the product.
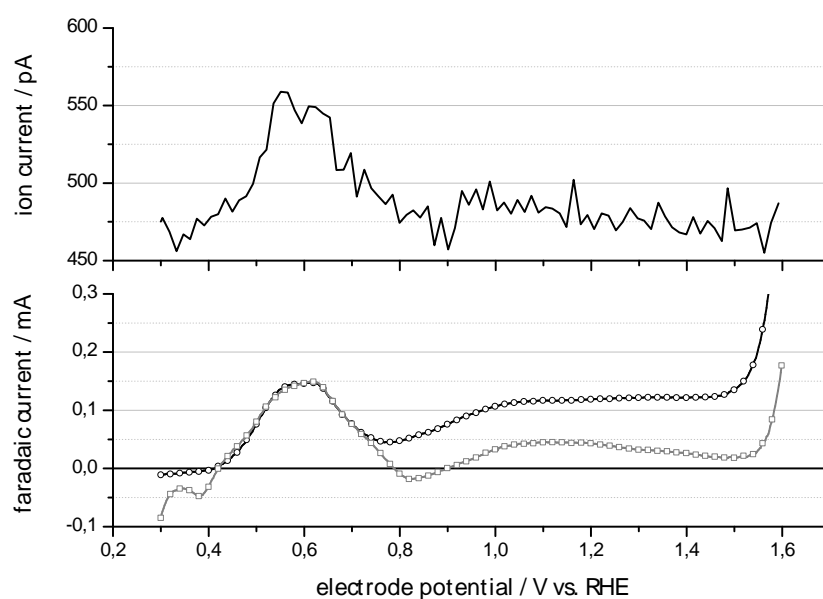

Figure 1: **Oxidation of adsorbed ethanol at platinum in 0.1 M KOH: Mass spectrometric ion current m/z 44, first anodic potential sweep (black line), Faradaic current, first anodic potential sweep (black circles), difference between the Faradaic current of the first and second anodic potential sweep (grey squares). Adsorption potential 0.3 V vs. RHE, adsorption time 5 minutes, scan rate 10 mV s^{-1}.**

However, if the stripping cycle is started in the cathodic instead of the anodic direction, the result differs significantly. Now in the low potential region the additional formation of methane is observed. The oxidation peak at about 0.6 V vs. RHE remains mainly unchanged whereas the oxidation peak at about 1.1 V vs. RHE has disappeared (cf. Figure 2).
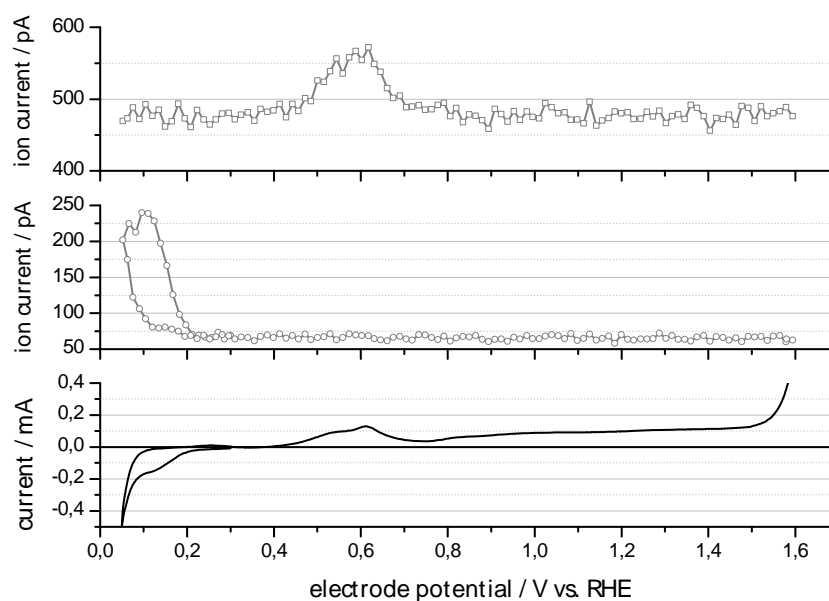
Figure 2: **Cathodically started stripping of ethanol adsorbates in 0.1 M KOH at platinum: mass spectrometric signal for carbon dioxide (m/z 44, grey squares), mass spectrometric signal for methane (m/z 15, grey circles) and Faradaic current of the first potential sweep (black line). Adsorption potential 0.3 V vs. RHE, adsorption time 5 minutes, scan rate 10 mV s^{-1}.**

It was further found that the stripping of CO under these conditions yields a single oxidation peak at about 0.6 V vs. RHE independent of the starting direction of the stripping cycle. Thus it can be concluded that the products formed by the adsorption of ethanol are CO_{ads} and $CH_{x,ads}$. The splitting of the C-C bond is therefore not hindered at a clean platinum surface, in agreement with the results found in literature for the acidic environment. However, in both cases the product composition changes in presence of bulk ethanol. This can be attributed to the poisoning of the electrode surface. The products released are acetaldehyde, acetic acid and ethyl acetate, both in the acidic and the alkaline environment. In the acidic environment the use of PtSn instead of Pt electrodes decreases the on-set potential for aldehyde formation but does not support the further oxidation of the acetaldehyde (cf. Figure 3 left) in agreement with literature[4]. However, it could be shown, that PtRu catalysts support the oxidation of acetaldehyde to carbon dioxide (cf. Figure 3 right).
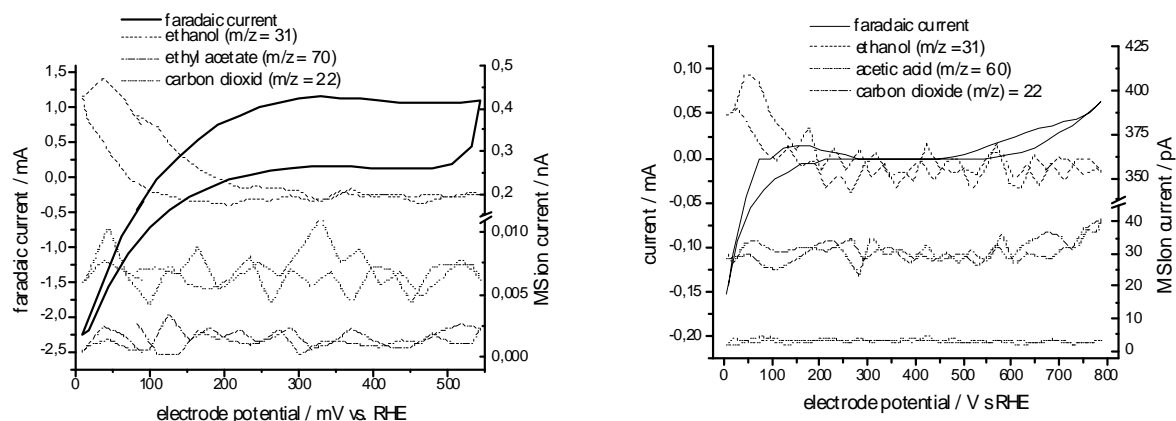
Figure 3: **MSCV of a platinum tin (3:1) electrode (left and a platinum ruthenium (3:19 electrode (right) in 0.1M acetaldehyde, 0.5 M sulfuric acid solution, CV (straight), ethanol (dashed), ethyl acetate (dash-dot) and carbon dioxide (dotted). MSCV was recorded at ambient temperature with a scan rate of 20 mVs⁻¹.**

In an alkaline environment the use of a palladium instead of a platinum catalyst can strongly increase the achievable current densities (cf. Figure 4).
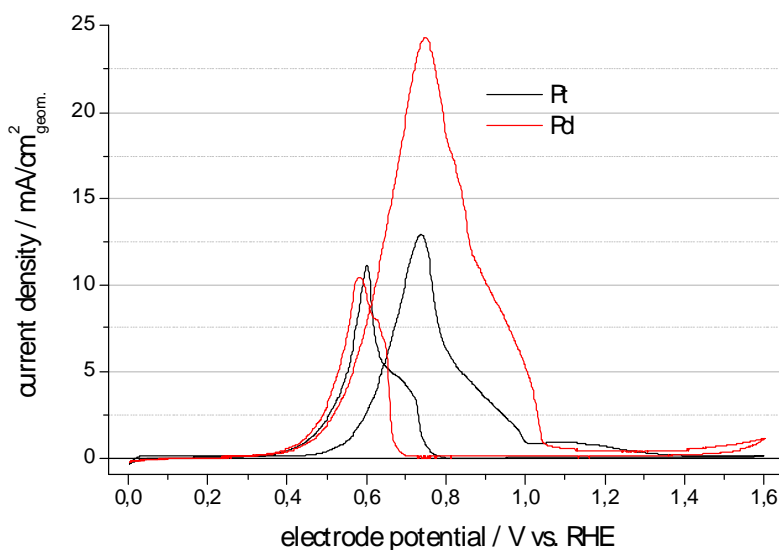

Figure 4: **Cyclic voltammograms of ethanol oxidation in 1M ethanol, 0.1M KOH solution at a platinum and a palladium electrode, respectively.**

Also some non-noble metals are active for ethanol oxidation under alkaline conditions (cf Figure 5). Details on the electrochemical investigations can be found in some recent publications[5-8].
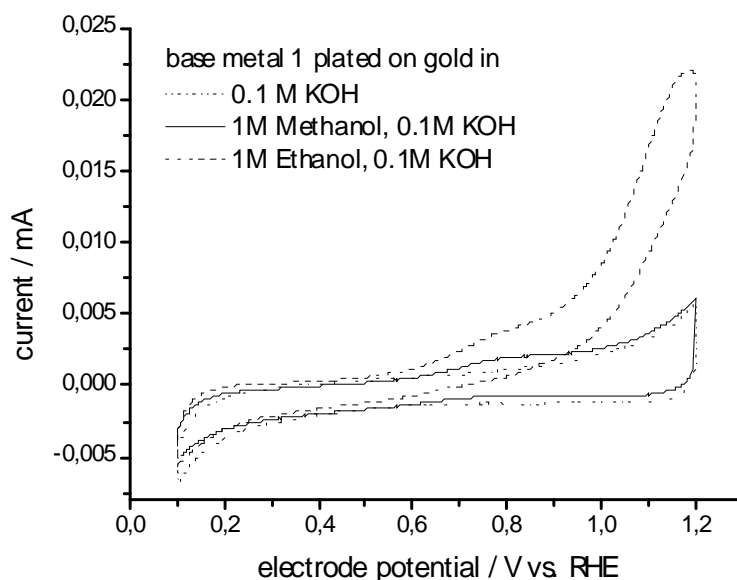
Figure 5: **Activity of a base metal electrode for the oxidation of ethanol and methanol in KOH solution at ambient temperature.**

3   Membrane Electrode Assemblies and Single Cell Results

Using the findings that PtRu, in contrast to PtSn, can catalyse the oxidation of intermediately formed acetaldehyde, a concept for an electrode layer containing both catalysts was developed. It was shown that the use of mixed anodes does increase the performance of the cell compared to cells that use only PtSn catalyst at the same catalyst loading (cf. Figure 6) and that the yield of carbon dioxide is increased even at a decreased catalyst loading (cf. Figure 7).
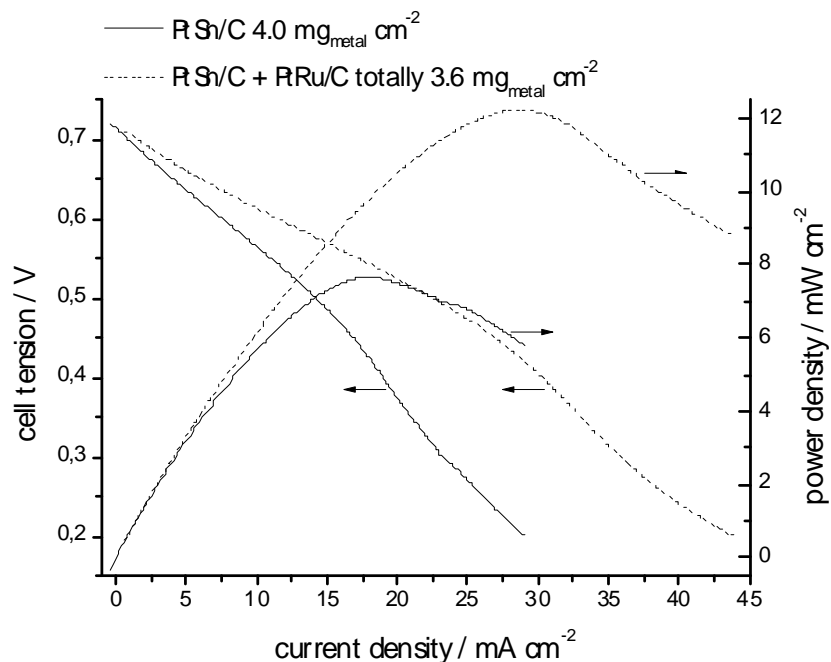
Figure 6:   **i-V and i-p properties of two different DEFC MEAs, with either Pt₃Sn/C or a mixture of Pt₃Sn/C and PtRu/C as anode layer, recorded at 50 °C, anode feed 1.5 ml/min 1 M ethanol solution, cathode feed 1 l/min synthetic air, scan rate 1 mVs⁻¹.**

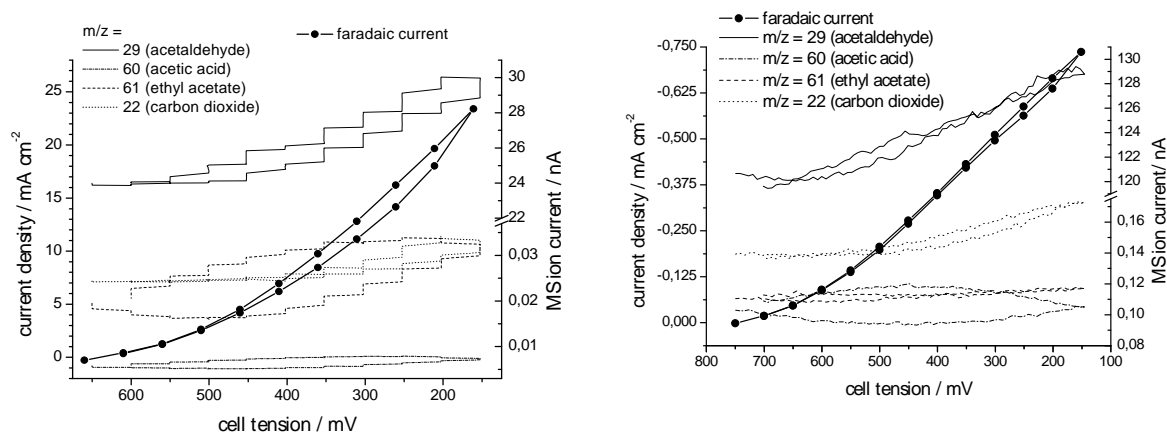
Figure 7:   **U-I curve and online MS-data for ethanol conversion in a DEFC with Pt₃Sn/C anode with 3.4 mg$_{metal}$/cm² (left) and DEFC with mixed Pt₃Sn/C and PtRu/C anode with 1.8 mg$_{metal}$/cm² (right) recorded at 40 °C, 2.0 ml/min 1 M ethanol.**

This approach is protected by German patent 10 2007 031 526 with worldwide patents pending.

Combining this approach with a new sPEEK based mixed matrix membrane developed by Fraunhofer IGB[9, 10] results in membrane electrode assemblies able to operate at close to ambient temperature with low cathode airflow rates[11] (cf. Figure 8)
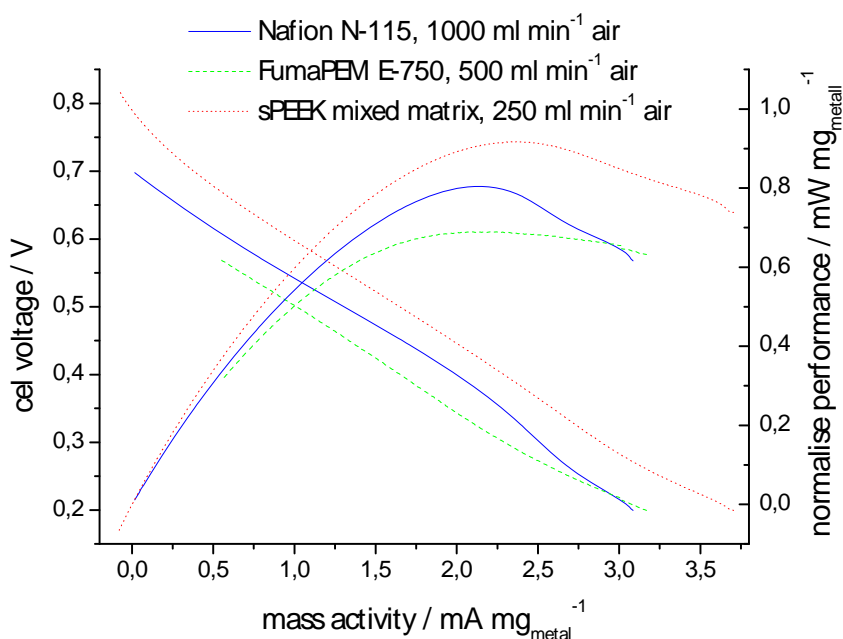
Figure 8:   **Comparison of the catalyst mass normalized performance values of MEAs with three different types of electrolyte at 30 °C. Air flow is set to the minimum useful value with the respective membrane.**

These cells operate very stably, however their performance is more suitable for small power applications, such as small portable appliances or remote sensors. The performance can be increased using alkaline fuel cells (cf. Figure 9). Using commercially available materials, power densities of > 100 mW cm^{-2} were achieved at 50 °C without cell optimisation.
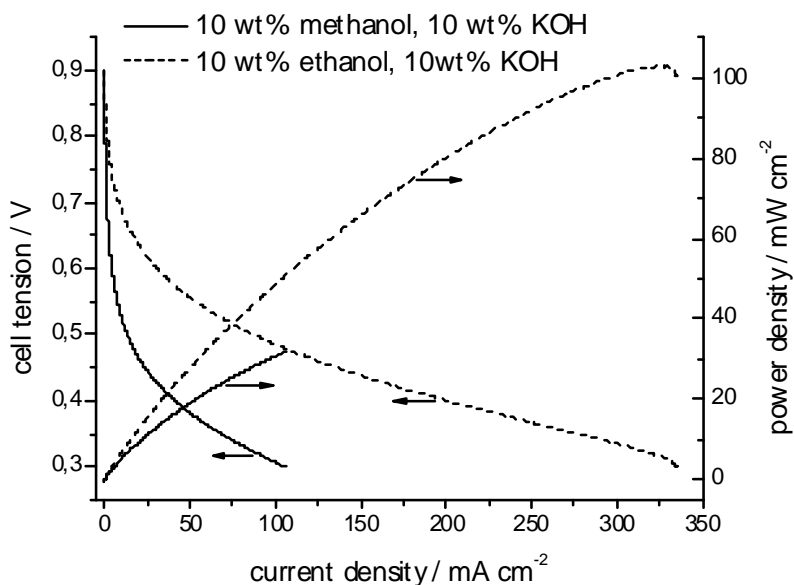

Figure 9:   **i-V curves of an AEM based DAFC with fumatech Fumasep membrane and Acta Hypermec electrodes operated at 50 °C and with synthetic air as oxidant. Fuel was either methanol or ethanol.**

The alternative way to increase power densities could be an increase of the operating temperature. So it could be shown that the performance of Nafion® based DEFC is increased significantly by increasing the operating temperature to 80 °C.
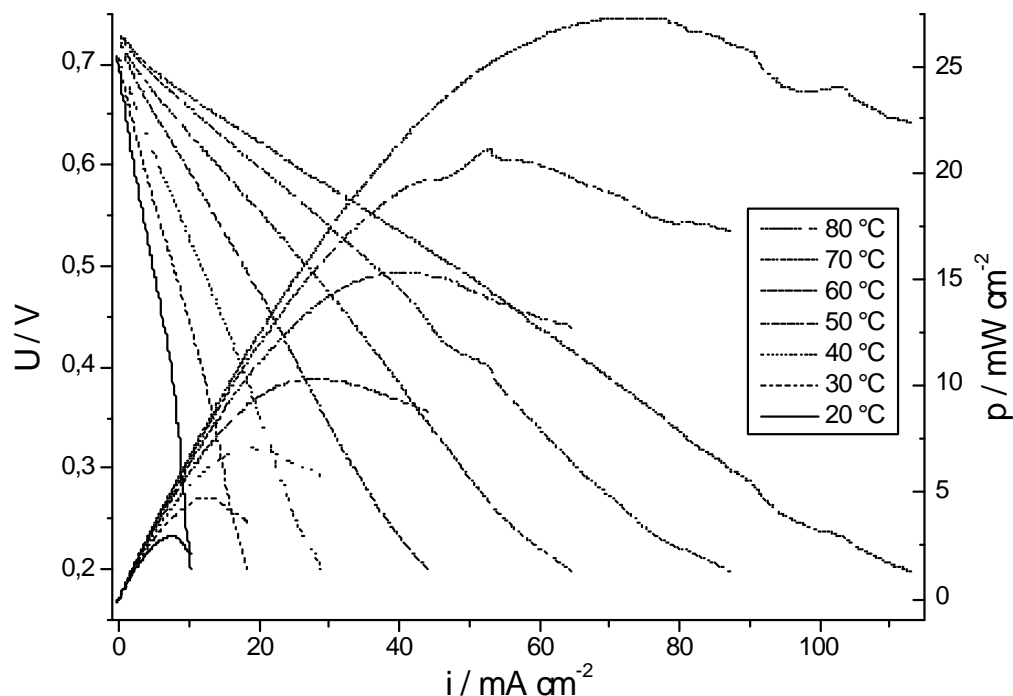

Figure 10: **I-V curves of a DEFC MEA with Nafion N-115 electrolyte, PtCo/C cathode with 2.3 mg cm^{-2} loading and a mixed PtSn/C PtRu/C anode with 3.6 mg cm^{-2} loading, operated with 1 M ethanol at 1.5 ml min^{-1} and air at 1000 mlmin^{-1}.**

A further increase of the operating temperature could therefore be a suitable option. First reports in literature on DEFC using either PBI/H$_2$SO$_4$ MEA[12] or PBI/KOH MEA[13] are quite encouraging.

4   Conclusions

The results show that the splitting of the C-C bond in ethanol is only hindered by the poisoning of the catalysts. An optimization of the catalyst to avoid the poisoning effects should be possible. As the oxidation the adsorbed CO$_{ads}$ and CH$_{x,ads}$ species requires the availability of   oxygen at the catalyst surface working at high pH levels will be beneficial as the oxygen availability increases with the pH. Alternatively, further increasing the reaction temperature should also help to avoid electrode poisoning. Thus DEFC in the kW power scale should be feasible.

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