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# Development of Palladium and Platinum Based Membrane Electrode Assemblies and Performance Characterization in the Alkaline Direct Ethanol Fuel Cell

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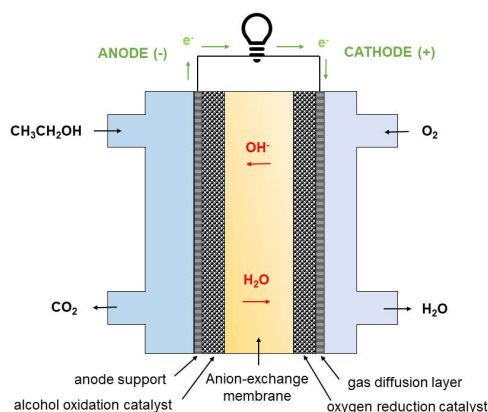
**Keywords:** Alkaline direct ethanol fuel cell, ethanol oxidation reaction, membrane electrode assembly.

## Abstract

Alkaline direct ethanol fuel cells (ADEFCS) have gained much attention in the last years due to their use of alternative energy sources. Commercial carbon supported palladium and platinum catalysts were ex-situ characterized by means of cyclic voltammetry experiments for their application in ADEFCS. The activity for the ethanol oxidation reaction (EOR) of the Pd/C catalyst was analyzed and an electrochemical active surface area (ECSA) of 411 cm<sup>2</sup> mg<sup>-1</sup>, an onset potential of 0.255 V and a maximum current density for the forward scan of 126 mA cm<sup>-2</sup> was examined. In addition, the performance of the Pt/C catalyst for the oxygen reduction reaction (ORR) was investigated resulting in an onset potential of 0.95 V and a limiting current density of -3.68 mA cm<sup>-2</sup> at 2000 rpm. Moreover, in-situ characterization in a self-designed ADEFCS was performed. Therefore, a membrane electrode assembly (MEA) was developed using the Pt/C catalyst as active cathode material, Pd/C as active anode material and a commercial fumasep® FAA-3-PK-130 as anion-exchange membrane. The results of the single cell tests showed that a humidified oxygen flow rate of 20 mL min<sup>-1</sup> and an ethanol fuel flow rate of 200 mL min<sup>-1</sup> are most optimal for a good performance of the fuel cell. A maximum power density of 0.4 mW cm<sup>-2</sup> was achieved.

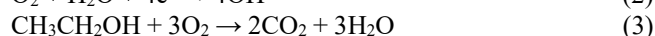
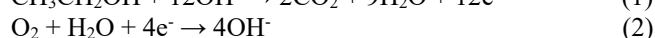
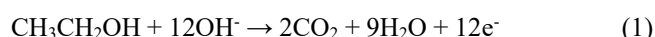
## Introduction

In the last decades alkaline direct ethanol fuel cells (ADEFCS) have gained much attention due to their robustness, low toxicity, easy storage and transport, environmental friendliness and low costs [1, 2]. The use of an alkaline electrolyte compared to an acidic one results in enhanced kinetics of the oxygen reduction reaction (ORR) and ethanol oxidation reaction (EOR), in a simpler water management and also in reduction of ethanol-crossover, due to the reversed dragging force of moving ions in anion exchange membranes (AEM) [3–6]. Figure 1 shows a schematic illustration of an ADEFCS with AEM, anode and cathode.



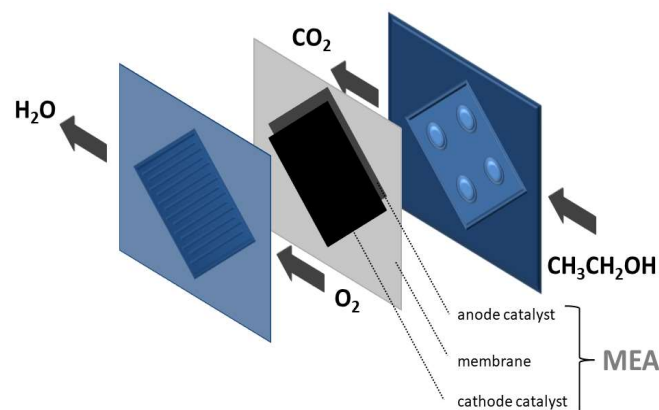
**Figure 1:** Working principle of the alkaline direct ethanol fuel cell.

The oxidation of ethanol takes place at the anode (1), while the oxygen is reduced at the cathode (2). The generated moving ions and the water are transported through the membrane. The electrons pass through an external circuit. The combination of EOR and ORR results in the overall reaction of the ADEFCS (3) [3, 7, 8].



Nowadays, Pd/C catalysts are the most used anode catalysts in ADEFCS, due to their high activity for EOR. The advantages are their higher stability, lower susceptibility to poisoning and higher oxophilic character in comparison with Pt/C and Au/C catalysts [9, 10]. Pt/C is also very active for the ORR in ADEFCS and is therefore widely used even though it's disadvantages like the high costs and the nonexistent ethanol tolerance [3, 11]. In ADEFCS, solid polymer electrolytes consisting of a hydrophobic backbone with positive functional hydrophilic groups are used as AEMs. The conduction of the ions through the membrane takes place by interaction with these hydrophilic groups. Furthermore, AEMs also act as selective barriers [12].

In general, the cathode, the anode and the AEM together are classified as membrane electrode assembly (MEA) (Figure 2). There are two different ways of MEA construction and building. The distinction is made on the basis of the catalyst coated surface, either membrane or gas diffusion layer (GDL). In the catalyst coated on membrane (CCM) method the membrane is coated, while in the catalyst coated on substrate (CCS) method a gas diffusion layer is utilized. The CCM is assembled together with both GDLs in the cell. In the CCS method, the preparation of both electrodes is separately performed. The AEM is afterwards hot pressed between both electrodes [13].



**Figure 2:** Schematic illustration of the membrane electrode assembly of the alkaline direct ethanol fuel cell.

For the preparation of the MEA, independent on the method, a well dispersed catalyst ink, to produce a uniformly

distributed catalyst layer without cracks, is essential. An important ingredient of this ink represents the ionomer. It creates the pathway for the ion transport between membrane and catalyst layer. Therefore, it influences the performance of the cell. Besides the choice of ionomer, the catalyst loading also plays a crucial role.

In this study, a Pd/C and Pt/C catalyst were electrochemically characterized using a typical three electrode set-up. The performance of the catalysts was also tested in a self-designed fuel cell, therefore MEAs were prepared. Different fuel flow rates on cathode and anode were used to determine the influence on the cell performance.

### Materials and Methods

**Materials.** Alumina suspension ( $\text{Al}_2\text{O}_3$ , 0.05  $\mu\text{m}$ , MasterPrep Bühler), Nafion® Solution (5 wt% in  $\text{H}_2\text{O}$ , Quintech), Propanol-2 (Isopropanol, 99.9 % p.a., Roth), Ethanol (EtOH, 99.9 % p.a., Roth), Potassium Hydroxide (KOH, 1.0 M Fixanal 1 L Ampoule, Sigma Aldrich), fumion® FAA-3 solution (10 wt% in NMP), fumasep® FAA-3-PK-130 (anion-exchange membrane, reinforced), comm. Pd/C (40 wt% on Vulcan from FuelCellStore), comm. Pt/C (40 wt% on carbon black from FuelCellStore).

**Electrochemical Characterization.** Both purchased catalysts, the EOR (Pd/C) as well as the ORR (Pt/C) catalyst were electrochemically characterized in a typical three electrode assembly. As working electrode, a rotating disk electrode (RDE) from PINE Research Instrumentation (AFE5T0GC) was used. This RDE was polished with an  $\text{Al}_2\text{O}_3$  suspension and cleaned with ultrapure water between the measurements. A reversible hydrogen electrode (RHE; Hydroflex®, gaskatel) as reference electrode and a platinized titanium rod (Bank Elektronik – Intelligent controls GmbH) as counter electrode were utilized. The Software and the Reference 600TM Potentiostat/Galvanostat/ZRA from GAMRY Instruments were used for data analysis.

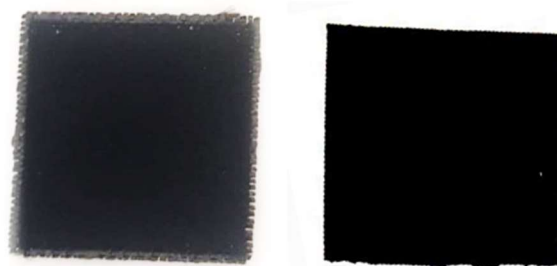
For the EOR measurement of the comm. Pd/C catalyst a suspension consisting out of catalyst, ultrapure water, 2-propanol and a small amount of binder (Nafion® ionomer solution) was prepared. The suspension was dispersed in an ultrasonic bath and afterwards pipetted on the working electrode. The RDE was rotated until an evenly distributed catalyst layer was formed. The measurements were performed in de-aerated 1 M potassium hydroxide solution, as well as in a mixture of 1 M potassium hydroxide and 1 M ethanol solution at 30°C.

The working electrode for the ORR measurements was similarly prepared as described for the EOR measurement, but ethanol was used for the slurry preparation instead of 2-propanol. The electrolyte solution (1 M potassium hydroxide solution) was purged with pure oxygen to carry out linear sweep voltammograms at different rotation rates of 400, 600, 900, 1200, 1600, 2000 rpm to describe the oxidation reduction reaction.

**Membrane Electrode Assembly Preparation.** For the investigation of the performance of the catalysts in the fuel cell, membrane electrode assemblies were prepared. Therefore, an automatic ultrasonic spray coater was used for depositing catalyst ink suspensions onto both different GDLs. Both catalyst ink suspensions consisted of catalyst, ultrapure water, 2-propanol and the anion exchange ionomer (fumion® FAA-3 solution).

The anode and the cathode showed a metal loading of 1  $\text{mg cm}^{-1}$ . At the anode side, a carbon cloth (ELAT - Hydrophilic Plain Cloth) and on the cathode side, a carbon paper (Sigracet 29 BC) was used as GDL (Figure 3). The fumasep® membranes were pretreated with 1 M KOH for 24 h and afterwards washed with ultrapure water. The

activated membranes were placed, without hot pressing, between the electrodes to prepare the membrane electrode assemblies.



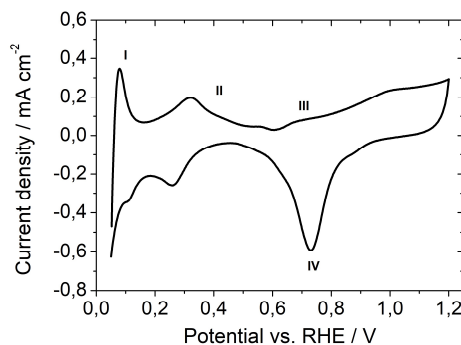
**Figure 3:** Spray coated carbon supported active layer (Pd/C comm. + FAA3 ionomer) on carbon cloth (ELAT-Hydrophilic Plain Cloth) (left) and (Pt/C comm. + FAA3 ionomer) on carbon paper (Sigracet 29 BC) (right).

**Single Cell Tests.** The prepared MEAs were assembled in a self-made ADEFC. Humidified oxygen gas was used as cathode feed gas, while a mixture of 1 M potassium hydroxide and 1 M ethanol solution was utilized as anode fuel. Different flow rates of 20, 50, 100 and 200  $\text{mL min}^{-1}$  on both sides were used to determine the influence on the cell performance. All single cell measurements were performed at room temperature. The cell potentials (V) and current densities (I) were recorded using a Zahner IM6ex Potentiostat. The obtained results are shown in a current density vs. potential diagram and furthermore, the calculated power densities are plotted in a power density vs. current density diagram.

### Results

In this section, the EOR performance of the Pd catalyst (Figure 4 and 5) and the ORR performance of the Pt catalyst (Figure 6 and 7) determined via electrochemical characterization are discussed. Furthermore, the influence of the flow rates of both fuels in the single cells with the self-prepared MEAs, consisting of the catalysts characterized before, is described. The investigation of the self-designed cell performance is shown in Figure 8 and 9 and in Table 1.

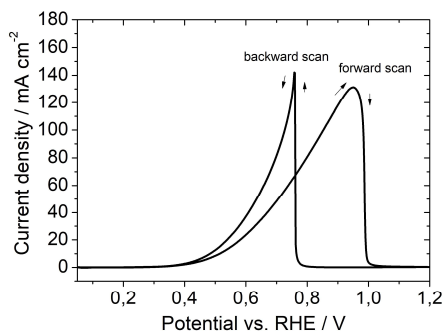
To get information about the typical oxidation and reduction reactions at the Pd surface, a CV of the Pd/C catalyst was recorded (Figure 4). The first peak (I) can be associated with the adsorption/absorption of hydrogen on Pd, while the second peak (II) showed the desorption of hydrogen. The formation of Pd oxide can be linked to peak (III), the characteristic reduction peak (IV) between 0.6 V and 0.8 V showed the reverse reaction to Pd [14]. Through integration of this peak, the electrochemical active surface area (ECSA) with a value of 411  $\text{cm}^2 \text{mg}^{-1}$  was determined.



**Figure 4:** CV of Pd/C in de-aerated 1 M KOH solution.

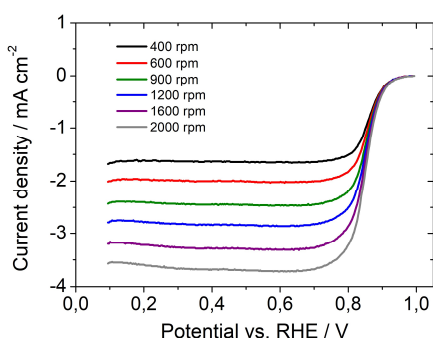
The onset potential and the maximum current density of the forward scan in the CV of the EOR (Figure 5) were used to

determine the activity of the catalyst. The Pd/C catalyst showed an onset potential of 0.255 V and a maximum current density for the forward scan of 126 mA cm<sup>-2</sup>. Therefore, the catalyst is suitable for catalyzing the EOR.



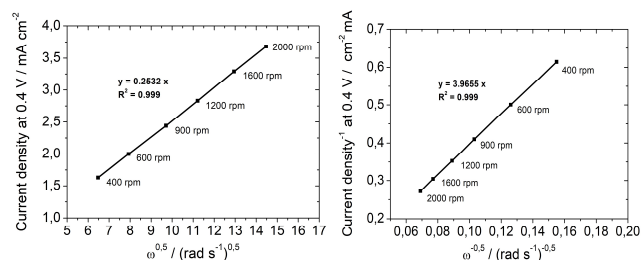
**Figure 5:** CV of Pd/C in a mixture of 1 M KOH and 1 M EtOH solution.

For the investigation of Pt/C's activity concerning ORR the voltammograms are illustrated in Figure 6. The onset potentials of all curves at a current density value of -0.05 mA cm<sup>-2</sup> were at 0.95 V, since current densities in this region are controlled by electron-transfer kinetics and are not influenced by the rotation rates [15]. Furthermore, the following limiting current densities were determined: -1.63 mA cm<sup>-2</sup> (400 rpm), -2.00 mA cm<sup>-2</sup> (600 rpm), -2.44 mA cm<sup>-2</sup> (900 rpm), -2.83 mA cm<sup>-2</sup> (1200 rpm), -3.29 mA cm<sup>-2</sup> (1600 rpm) and -3.68 mA cm<sup>-2</sup> (2000 rpm).



**Figure 6:** ORR voltammograms of Pt/C in O<sub>2</sub> saturated 1 M KOH at different rotation rates.

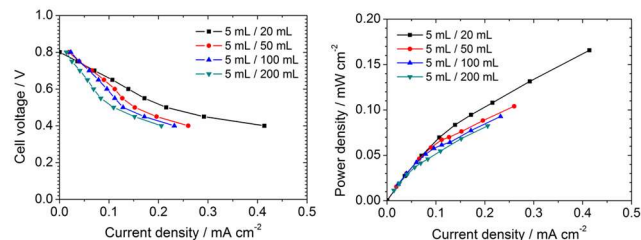
Levich and Koutecky-Levich plots were used for the determination of the number of electrons, which are exchanged during the oxygen reduction reaction. The limiting current densities at 0.4 V were utilized for the Levich and Koutecky-Levich analysis [15]. Figure 7 illustrates both plots for the calculation. The determined transferred electron number, between 3.6 and 3.7, is lower than the theoretical value of 4, because of the production of the intermediate H<sub>2</sub>O<sub>2</sub> [16]. Therefore, Pt/C is suitable for the ORR at the cathode.



**Figure 7:** Levich plot (right) and Koutecky-Levich plot (left) of Pt/C.

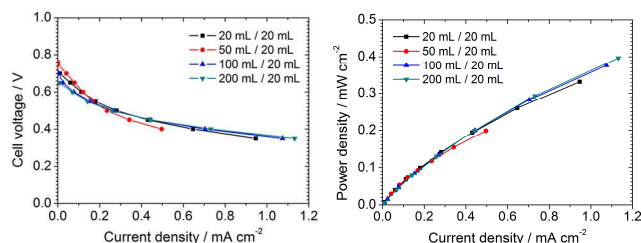
After the successful electrochemical characterization of both catalysts in half cell experiments, MEAs were prepared

and single cell tests performed. To determine the influence on the cell performance and to find the optimal fuel flow rate, different flow rates of 20, 50, 100 and 200 mL min<sup>-1</sup> on both sides were tested. In Figure 8 and Table 1, the influence on the cell performance of the varying oxygen flow rate can be seen. It was determined that with increasing oxygen flow rate the cell performance decreases. Therefore, a humidified oxygen flow rate of 20 mL min<sup>-1</sup> is most optimal.



**Figure 8:** Current density vs. potential diagram (right) and power density vs. current density diagram (left) using different oxygen flow rates at room temperature.

The same experiment was afterwards performed with different ethanol fuel flow rates, while the oxygen flow was set to the before determined value of 20 mL min<sup>-1</sup>. The variation and the influence can be seen in Figure 9 and Table 1. The behavior is vice versa, with increasing ethanol fuel flow rate a higher performance was reached. The maximum power density of 0.4 W cm<sup>-2</sup> was achieved with an ethanol fuel flow rate of 200 mL min<sup>-1</sup> and a humidified oxygen flow rate of 20 mL min<sup>-1</sup>.



**Figure 9:** Current density vs. potential diagram (right) and power density vs. current density diagram (left) using different ethanol fuel flow rates at room temperature.

**Table 1:** Results of the single cell tests.

Fuel flow rates mL min <sup>-1</sup>	Maximum power density / mW cm <sup>-2</sup>	
	O <sub>2</sub> *	EtOH**
20	0.17	0.33
50	0.11	0.20
100	0.09	0.38
200	0.08	0.40

\*constant EtOH flow rate of 5 mL min<sup>-1</sup>

\*\*constant O<sub>2</sub> flow rate of 20 mL min<sup>-1</sup>

## Conclusion

Palladium and platinum-based carbon supported catalyst were electrochemically characterized in half cell experiments for the use in ADEFCs. The commercial Pd/C catalyst was found out to be capable of catalyzing the EOR at the anode, while the commercial Pt/C is suitable for the ORR at the cathode. Following results were determined for the Pd/C catalyst: an ECSA of 411 cm<sup>2</sup> mg<sup>-1</sup>, an onset potential of 0.255 V and a maximum current density for the forward scan of 126 mA cm<sup>-2</sup>. The investigation of the Pt/C catalyst resulted in an onset potential of 0.95 V and a limiting current density of -3.68 mA cm<sup>-2</sup> at 2000 rpm. Moreover, the number of transferred electrons was determined to be between 3.6 and 3.7. A MEA was developed using these two catalysts and inserted into a self-designed ADEFC. The results of the single

cell tests show that a humidified oxygen flow rate of 20 mL min<sup>-1</sup> and an ethanol fuel flow rate of 200 mL min<sup>-1</sup> are most optimal for a good performance of the fuel cell. A maximum power density of 0.4 mW cm<sup>-2</sup> was achieved.

### Acknowledgement

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