Int. J. Electrochem. Sci., 15 **(2020)** 6035 – 6040, doi: 10.20964/2020.07.12

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Cathode Supported Hybrid Direct Carbon Fuel Cells with Different Anodes

K. Kammer Hansen[1,*], *L. Deleebeeck*, *V. Gil*[1,2]

[1] Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800, Kgs. Lyngby, Denmark
[2] ARAID Foundation and Foundation for the Development of New Hydrogen Technologies in Aragón, Spain,
[*]E-mail: kkha@dtu.dk

Received: 5 February 2020 / *Accepted:* 29 March 2020 / *Published:* 10 June 2020

Three different types of hybrid direct carbon fuel cells were investigated for direct electrochemical oxidation of carbon black. One where anode-supported with a Ni/YSZ (yttria stabilized zirconia) anode and two cathode supported cells with either a NI/YSZ anode or a praseodymium-doped cerium oxide anode. The middle one performed the best, probably due to better contact to anode with the fuel and the presence of metallic nickel.

Keywords: Carbon black oxidation, HDCFC, Cathode supported, CPO, Ni-YSZ

1. INTRODUCTION

The direct carbon fuel cell is a convenient way of converting carbon containing material into electricity without combustion, with a very high theoretical efficiency, up to 100%. In practice up to 80% has been achieved [1]. Another advantage is that air and fuel not is mixed in the process but separated by an ionic conducting electrolyte. This results in an exhaust containing no NOx and almost pure CO_2 ready for sequestration.

Several different types of direct carbon fuel cells exist, among them the hybrid direct carbon fuel cell (HDCFC) [2]. The HDCFC is a hybrid between a molten carbonate fuel cell (MCFC) and a solid oxide fuel cell (SOFC). The HDCFC is made by adding alkaline carbonates to the anode chamber of a SOFC. When the HDCFC is operated at temperatures where the carbonate is molten the reaction zone between solid carbon and the anode is increased. Anode supported SOFC's are state of the art. Here cathode supported cells with two different anodes are fabricated, tested and compared with a conventional anode supported SOFC. Direct carbon oxidation is desired as it has the highest theoretical

efficiency. The problem with anode supported cells are that the carbon not is in direct contact with the active anode, see figure 1. This results in indirect oxidation of carbon;

(1) $CO_2 + C \rightarrow 2CO$

(2) $CO + O^{--} \rightarrow CO_2$,

With a much lower efficiency than the full direct oxidation given in (3)

(3) $C + O^{--} \rightarrow CO_2$, E = 1.02 V, vs. Air

The oxidation given in (2) has an OCV higher than (3), up to 1.4 V vs. air. The advantage of using a cathode supported cell is sketched in figure 2. Here it is seen than the carbon is in direct contact with the active anode.

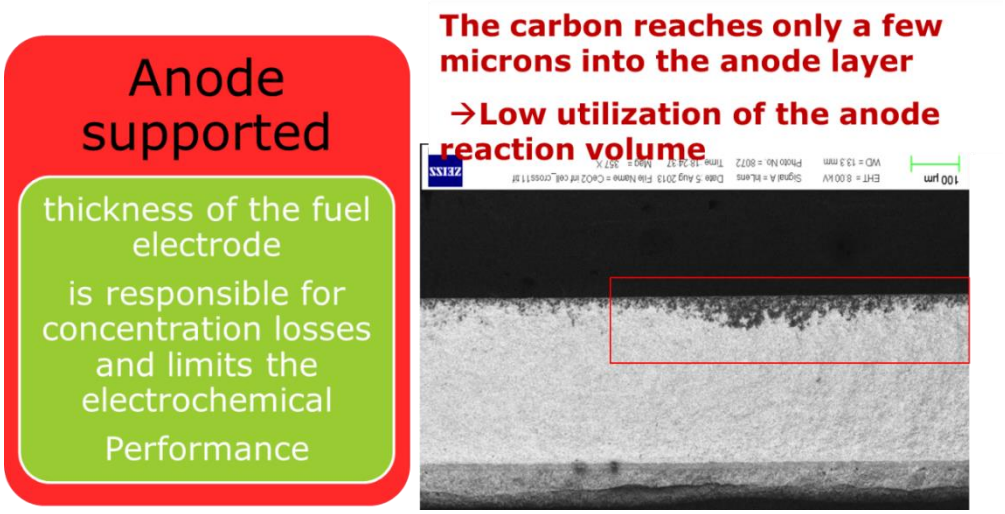


Figure 1. Micro-graph of an anode supported cell showing the penetration of the support with carbon in top of the anode support.

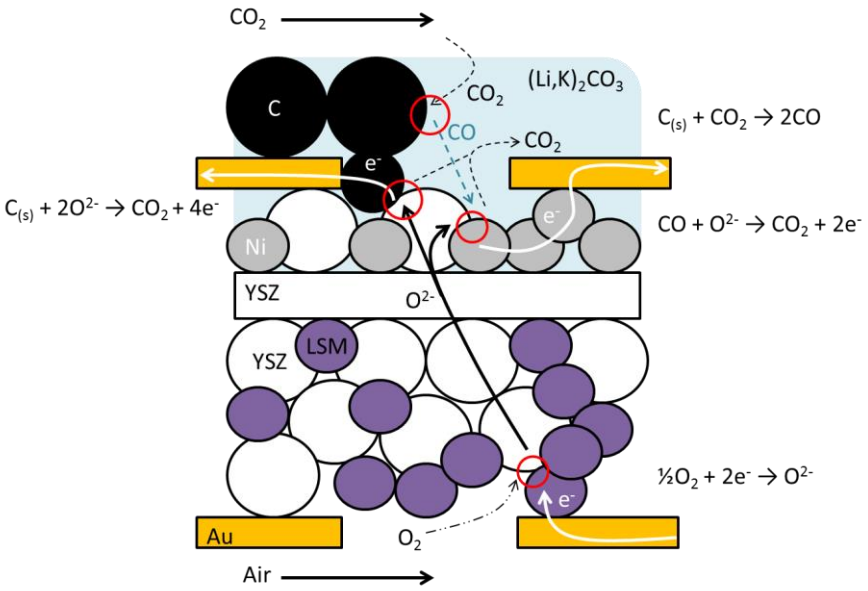
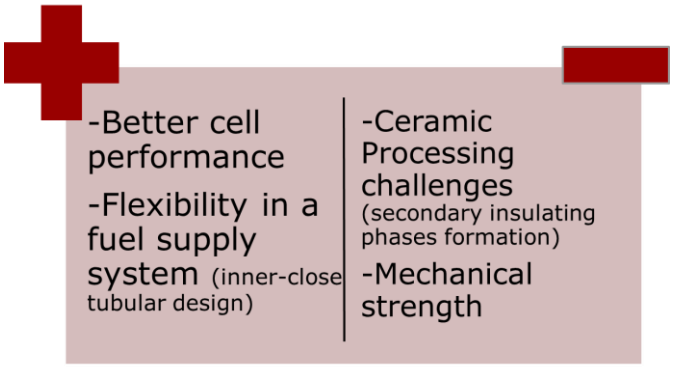


Figure 2. Sketch of a cathode supported cell, showing the direct contact between the active anode and the carbon fuel.

This makes possible the direct full oxidation of carbon, utilizing the full potential of the direct carbon fuel cell. The main advantages and difficulties with a cathode supported DCFC is listed in table 1. Among the disadvantages is difficult processing and low mechanical strength.

Table 1. Strengths and weaknesses of the cathode supported concept is listed in the table.



Besides the conventional Ni/YSZ anode other types of anodes has also been tested, see i.e. [2-7]. The results shown in these works is that the alternative anodes can have a very high performance. One example is the Fe-Mo double perovskite, giving a power density of approximately 400 $mWcm^{-2}$ at 800 ^oC [3-4]. Another one is the Ni-Ce-Mn-Fe-oxide with a peak power density of 580 $mWcm^{-2}$ at 800 ^oC [5]. The microstructure of the anode is also very important [. This has been shown, by making anodes by soaking the anode material into a textile before firing [6, 7]. This gave record high peak power densities of 325 $mWcm^{-2}$ at 600 ^oC [6].

2. EXPERIMENTAL

Cathode supported cells with the two different types of anodes were fabricated and tested together with a conventional anode supported SOFC. The two anodes were Ni/YSZ and CPO. Results of the first two is reported in [8] but is shown here for comparison as it gives strong new insight. The cells were fabricated as in [8].

The penetration of Carbon into the anode support was studied with scanning electron microscopy (SEM). The microscope used was a high-resolution field emission scanning electron microscope (FESEM, supra 35, Carl Zeiss, Germany) with an energy dispersive spectroscopy detector. Samples were vacuum embedded in Epofix (Struers, Denmark). The samples were then polished to 1 μm, before the micro-graphs were recorded.

The performance of the three different types of cells was evaluated in the following way. Experimental setup is described in [8 and 9].

The HDCFC fuel, consisting of 4:1 wt% carbon black acetylene (C): (62-38 wt% Li-K)$_2CO_3$ (CO3) and was ball-milled together using medium ZrO_2 balls at a low speed for 3 hrs. Carbon black

acetylene (99.9+ % purity, Alfa Aesar) was used as received. The eutectic mxture Li_2CO_3-K_2CO_3 (Sigma Aldrich) was before that mixed for several hours by shaking vigorously.

The full-cell HDCFC and the Inconel cell house employed in cell testing [10] consists of an anode chamber (A), containing ~ 2 g fuel and a cathode gas flow plate (F). A total weight of 8 kg was put on top of the cell house during testing.

First the cells were heated to 800 ºC with 180 ºC. Gasses supplied were N_2 (5 L/hr, anode) and air (19 L/hr, cathode). After reduction of the NiO (~ 30 min) the cells were cooled to 755 °C and a mixture of 80-20 vol% N_2-CO_2 (6 L/hr total flow rate) was flushed in the anode chamber. I-V curves were recorded by varying the current load. The maximum power density was then calcultaed before plotting the data.

3. RESULTS

The problem with an anode cell configuration is shown in figure 1. Here it is seen that the carbon only penetrates the first few microns of the anode support. The results of the testing of the three different cells are given in figure 3.

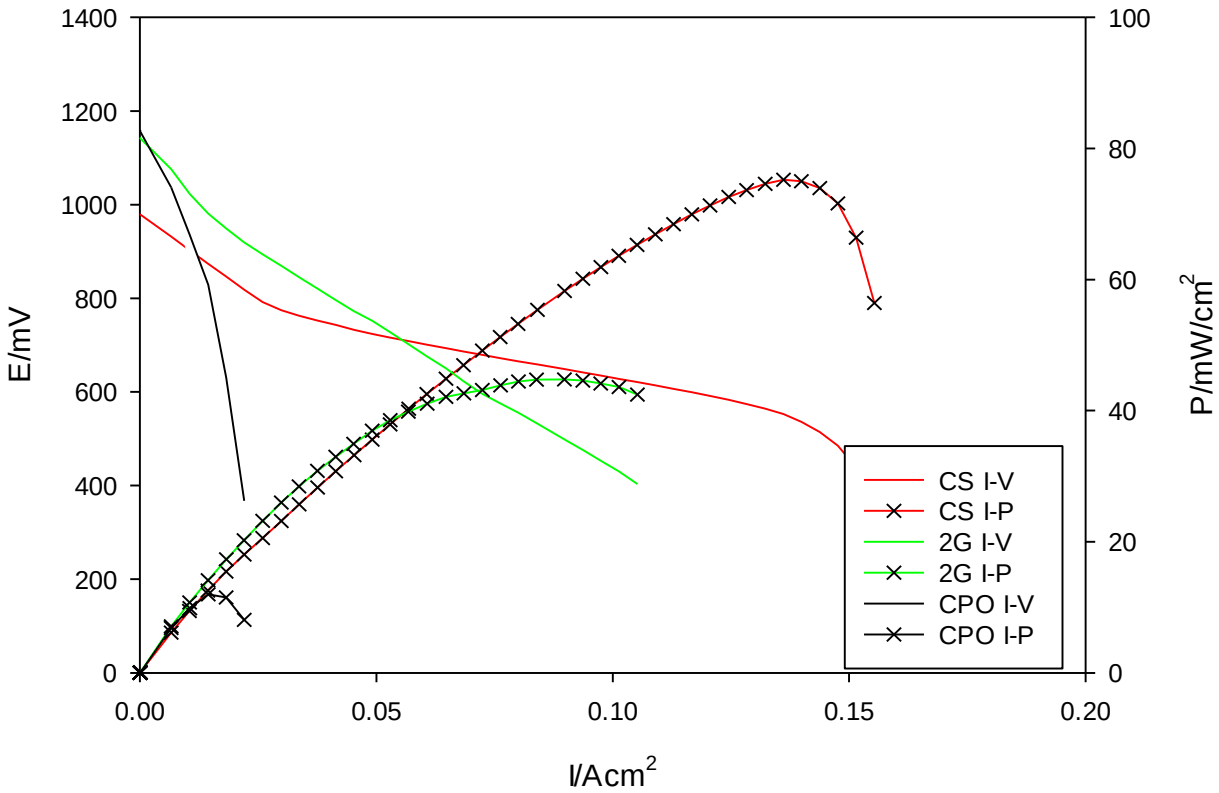


Figure 3. Performance of the three cells investigated in this study. The cathode supported cell, with the Ni/YSZ anode has by far the best performance.

Here the I-V and I-P curves are given at 800 ^{o}C. The far best performance is reached by the cathode supported cell with the conventional Ni/YSZ anode, followed by the anode supported cell and then, with the lowest performance, the cathode supported cell with full ceramic CPO anode. The maximum power density obtained 80 mWcm^{-2} and the highest current density is 0.15 Acm^{-2}. The cathode supported cell with the CPO anode has a very poor performance. The OCV is also different for the three types of cells. The OCV is highest for the anode supported cell and the cathode supported cell with the CPO anode, a little less than 1.2 V vs. air. The cathode supported cell with the conventional Ni/YSZ anode has an OCV around 1.00 V vs. air.

4. DISCUSSION

The OCV is higher for the anode supported cell with the conventional Ni/YSZ anode than for the cathode supported cell with a similar anode (see figures 1 and 2). This could be due to more direct oxidation of carbon in the case of the cathode supported cell, as the direct carbon oxidation has a lower OCV than the indirect oxidation of carbon [2]. This outlines the strength of using a cathode supported cell. In addition to this the performance of the cathode supported cell is also higher than for the anode supported cell. The performance of the cathode supported cell with the full ceramic CPO anode is lower than for the cathode supported cell with the conventional Ni/YSZ anode for which the OCV is lower. This indicates that a metal is needed in order to perform direct oxidation of carbon with a high performance. Further optimization of the cathode supported cell can improve the concept even further. Among the issues is the performance of the cathode. Better cathodes can be used in order to solve this issue. Alternative anodes as suggested in the literature [3-7] can also be used instead of the Ni/YSZ anode to obtain a higher performance. Together with an optimization of the microstructure this can give close to real world applications power densities.

5. CONCLUSION

Cathode supported direct carbon fuel cells can have a higher performance than conventional anode supported cells and achieve a higher degree of direct carbon oxidation. The choice of anode material is very important. This study points in the direction that a metal is needed in order to achieve a high performance for direct coal oxidation.

ACKNOWLEDGMENTS
The technical staff at DTU Energy is thanked for assistance.

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