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CsH₂PO₄ as electrolyte for the formation of CH₄ by electrochemical reduction of CO₂

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Abstract It has been shown that methane can be formed in high amounts by co-electrolysis of CO₂ and H₂O using a nickel cathode, a CsH₂PO₄-SiC composite electrolyte and an IrO₂ anode. The experimental conditions were 300 °C and 8 bar. The maximum efficiency close to 100% for methane was obtained at a current density of 10 – 15 mA/cm². A small amount of hydrogen was formed as the only other product.

Introduction

The excessive emission of carbon dioxide is at present one of the greatest problems for the world. Electricity will in increasing amounts have to be based on renewable energy resources. An interesting idea is to use wind and solar based electricity to reduce the emission of carbon dioxide and to turn the electric energy into valuable reduction products that can replace the fossil fuel resources.

The reduction of CO₂ in aqueous electrolytes (usually KHCO₃ solutions at room temperature and at atmospheric pressure) into methane - among other products - has attracted the interest of electrochemists and inorganic chemists for decades, as it has been understood that such a procedure can facilitate a sustainable low temperature redox cycle for energy storage and conversion.¹⁻³ The problems in this connection are perhaps best expressed by Kortlever et al.³: “However, major issues still need to be resolved before the reduction of CO₂ to fuels becomes appealing for technological applications. The main problems holding back electrocatalytic CO₂ reduction are the high overpotentials needed and the poor product selectivity and faradaic efficiency. The high overpotentials and poor product selectivities are the result of inappropriate adsorption energies of key reaction intermediates. The low faradaic efficiencies are due to the competition with the hydrogen evolution reaction (HER), which takes place in the same range of potentials as CO₂ reduction. Thus, new catalysts need to be developed that increase the product selectivity and efficiency of electrocatalytic CO₂ reduction while simultaneously lowering the overpotentials”.

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Hori et al.¹ discovered in 1985 that copper in aqueous KHCO₃ solutions has a unique ability to act as an effective catalyst for the electrochemical reduction of CO₂ to various hydrocarbons, such as methane and ethylene, and with good faradaic efficiencies in comparison to other catalysts. Since

then substantial efforts have been made to understand the special reactivity of copper for this reaction. It was shown in early works that CO is a key intermediate in the formation of hydrocarbons from the reduction of CO₂ on copper catalysts,⁴ a fact which is now widely accepted in the literature. Proposing a conclusive mechanism for the reduction of CO₂ on copper is however a challenge, as illustrated by the observation of 16 different products formed from CO₂.²

As mentioned above most of the measurements reported so far have been on aqueous KHCO₃ solutions at ambient pressure and with copper cathodes. However, there have also been reported experiments with the same electrolyte at high pressures and elevated temperatures and with a platinum gas diffusion electrode instead of the copper cathode. As expected due to the increased solubility of CO₂ in water at high pressures, the faradaic efficiency went up for the production of CH₄.⁵ There have also been attempts to produce methane at much higher temperatures using solid state proton conducting oxide electrolyzers but at atmospheric pressures. In most cases only CO, hydrogen and water were produced^{6,7} due to the high temperature (~600 °C) but in some cases small amounts of CH₄ were also reported.⁸

Our approach is to work both at moderately high temperatures (~350 °C) and elevated pressures (~30 bar). There are several advantages with this. The main advantage is that generally the overpotentials in electrochemical processes will be reduced at higher temperatures. A good example is the solid oxide electrolyzer functioning at around 1000 °C⁹ at which temperature there is almost no overpotential. It is a little more difficult to predict the effect of increasing the pressure but due to the Le Chatelier principle it is expected that when the number of molecules is smaller after reaction than before reaction an increase in pressure will promote the reduction. The question here is what molecular species at the cathode participate in the reaction: H₂ or H?¹⁰ Concerning the electrolyte not many hydrogen ion conducting liquids are stable against electrolysis at around 300 °C. Among the few ones that fulfill this purpose are phosphate melts. We have worked with these melts and shown that they can be used for electrolysis of water and that they have a reasonable conductivity.¹⁰⁻¹⁵ We have further shown that in order to stabilize the composition at higher temperatures it is necessary to keep a considerable water vapor pressure above the melts.^{13,14} A special interest is surrounding the CsH₂PO₄ salt which exhibits super-protonic conductivity in the solid state at above ~230 °C.¹⁶ This makes it more suited for producing highly conducting gastight membranes, for example for fuel cells.¹⁷⁻²⁰ In order to increase the mechanical strength of this electrolyte different researchers have added different oxides.¹⁸⁻²⁵ We think that there is a problem by using oxides as additives since the oxides probably slowly react with the H₂PO₄⁻ ions, thus decreasing the superconductivity.²⁶ In our case we therefore decided to use the more stable SiC instead of e.g. ZrO₂ as previously done in connection with a fuel cell operation.²⁰ We think the used CsH₂PO₄ electrolyte opens up possibilities for substituting the anode material IrO₂ with e.g. RuO₂-Ta₂O₅ composites²⁷ but since our concern was about the cathode we decided in this work to use IrO₂ as a safe material for the anode. We have already in a patent shown that methane can be formed by co-electrolysis of water and CO₂ with the solid super-protonic CsH₂PO₄ electrolyte.²⁸ We have also shown that hydrogen formation is substituted by another electrochemical process forming CH₄ in liquid CsH₂PO₄ at 350 °C and approximately 25 bar of water pressure.²⁹ The conditions then were not far from the conditions using solid CsH₂PO₄ which will be described in more detail in the following.

In the experimental part there is a further description on how we constructed the cell to examine the production of methane by electrochemical reduction of CO₂ and water with a CsH₂PO₄ membrane electrolyte and a nickel cathode.

Experimental

Electrolysis

The electrolysis setup is depicted in Figure 1. Three main components of the electrolysis setup are (A) the electrochemical cell, (B) the evaporator and (C) the heated outlet valve from the anode. These are all placed inside a closed container (D), i.e. an autoclave in order to allow for an external pressure on the same level as inside the system (A), i.e. ~8 bar. This was done in order to reduce the possible leaking from the electrochemical cell in case of lack of gasket tightness. The backpressure valve was set to open at a pressure of 8 bar. The setup was equipped with four electric heating elements, one for the evaporator, two for the electrolysis cell (one for each electrode compartment) and one for the outlet back-pressure valve, respectively. The heating elements are not shown. The temperature of the evaporator and of the back-pressure valve was set at values corresponding to the desired water vapor pressure or slightly above. For a desired pressure of 8 bar it meant 170 °C, as the boiling point of water at 8 bar is 170 °C. The temperature of the electrolysis cell was set at a higher temperature (300 °C).

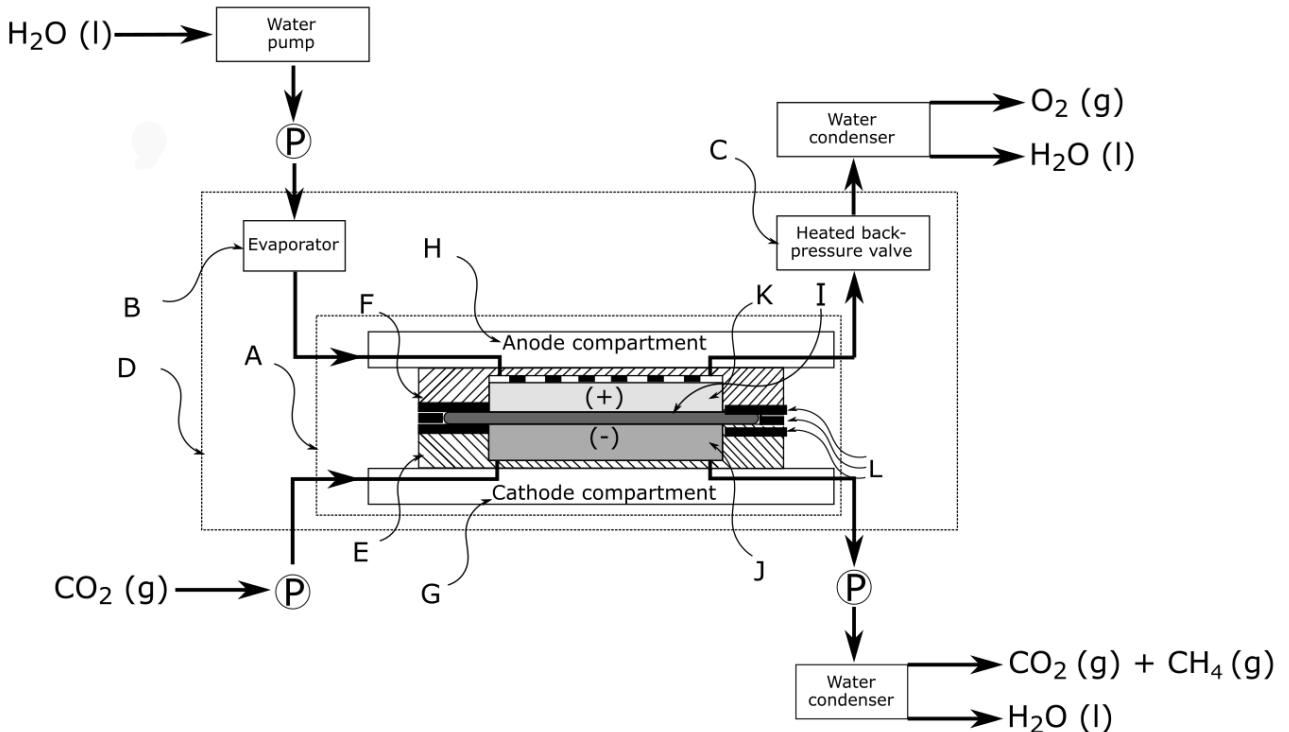


Fig. 1. Electrolysis setup. (A) Electrolysis cell. (B) Evaporator. (C) Back-pressure valve placed in a heated aluminum block. (D) Autoclave. (E) Cathode flow plate of stainless steel. (F) Anode flow plate with serpentine flow channel made of tantalum-coated stainless steel. (G and H) Electrode compartments/back plates of brass. (I) Electrolyte of CsH_2PO_4 and SiC powder. (J) Porous nickel cathode. (K) Anode – stainless steel felt coated with tantalum and sprayed with a slurry of IrO_2 and PBI-binder in formic acid (L). Gaskets made of polyimide (Kapton) and soft graphite material (Papytex). Pressures (P) were measured for the anode compartment at the water inlet, i.e. as the

pressure delivered by the water pump to keep up the flow, and for the cathode compartment at both the CO₂ inlet and the cathode outlet.

The cell consisted of a flowplate (E and F) and a backplate (G and H) for each electrode compartment. The electrolyte (I) and the electrodes (J and K) were placed between the flowplates. These were made of stainless steel (AISI316) for both cathode and anode (E and F), but the latter was coated with a 40 µm dense layer of tantalum made by chemical vapor deposition by the company Tantaline A/S (Denmark). Both the anode and the cathode flowplates had a spiral type flow pattern engraved. The back plates/compartments were made of a Cu alloy, (JM7-20, Johnson Metall AB (Sweden), composition in wt. %: Cu80Al10Fe5Ni5). The electric insulated heating elements were placed in good thermal contact with these plates, and the high conductivity of the alloy ensured a uniform temperature distribution.

The pressure was monitored with pressure measuring devices at various places in the system: At the HPLC pump (Shimadzu UFC, Japan) that pumped water into the cell and at the valve that controlled the CO₂ inlet. Furthermore, the pressure of the outlet from the cathode was measured before being mixed with a He-carrier gas and sent to a gas chromatograph for product identifications. Finally the internal autoclave pressure, surrounding the electrolysis cell (A), was measured and controlled via the nitrogen supply connected to the autoclave (D).

Operation of the electrolysis cell followed a standard procedure where the CO₂-flow was started as the first step. Then the heating elements were turned on and when the temperature was high enough to make sure that no water would be condensing in neither the cell nor the anode outlet valve (typically at 160 °C) the water pump was finally started.

The sealing of the cell towards the surroundings - as well as between anode and cathode chambers (L) - requires materials which at the same time provide necessary electrical insulation, flexibility and stability at the high temperature. This was obtained by using a 2-layer combination of Kapton foil (a polyimide) and Papyex (a flexible graphite material). Kapton is a thin (50 or 75 µm), non-compressible, but electrically insulating foil, whereas Papyex is a soft, flexible, but also conducting material, in thicknesses of 0.2 mm and 0.5 mm. The thickness of the combined gaskets were adjusted to fit to the thicknesses of the electrodes and the electrolyte by adding several multiple layers of Kapton and Papyex. It was attempted to keep the total initial thickness of the gaskets around 120-125 % of the thickness of electrodes in order to get a suitable compression of the Papyex. Concerning the Papyex layer around the edge of the electrolyte, it was chosen to have the same thickness as the thickness of the electrolyte before start of each experiment, as a densification of the electrolyte was happening when approaching the working temperature, thereby making it thinner, and thereby increasing the force applied on the Papyex, making it tight.

The produced gasses were analysed by a gas chromatograph (Agilent Technologies 7890B) using a TCD detector and a combination of Hayesep Q and Hayesep N columns. Helium was used as the carrier gas. The electrochemical measurements were done by a Versastat 3 potentiostat from Princeton Applied Research.

Composite electrolytes:

The electrolytes used were based on a mixture of CsH₂PO₄ and SiC powder reinforced with fibers of Polybenzimidazol (PBI) supplied by the company PBI Performance Materials, Bloomberg, USA.

Furthermore a small amount of 85 % phosphoric acid was added in order to generate a certain amount of a molten phase to facilitate the densification during the following heating. The addition of SiC, an inactive “filler material”, was done in order to help immobilizing this molten phase in the heat as well as the CsH₂PO₄ itself, which is known to be rather fluid when in the conductive superprotic state.¹⁴ An analogous procedure but in this case with a CsH₂PO₄-ZrO₂ composite electrolytes and without fiber-reinforcement was tested in a fuel cell that proved to be tight, but the ZrO₂ slowly reacted with the CsH₂PO₄^{20,26} as most other oxides probably will do at higher temperatures. In the present work the electrolyte was applied/added in a shape as a pressed disk of larger diameter (diameter 42 mm) than before, and that was far beyond what was possible to do by ordinary pellet pressing. To make the pellet coherent therefore fiber reinforcement by PBI fibers was introduced to improve the mechanical strength of the material, thus making it possible to handle the large electrolyte discs.

CsH₂PO₄ was prepared as described by Nikiforov et al.¹⁴ Before use, however it was mechanically ground using an effective kitchen coffee grinder. PBI felt was supplied by PBI Performance Materials, Bloomberg, USA (type SL 40g/cm² 100% PBI). SiC of particle size 0.1 – 1.0 µm, alpha form, purity 99 % was obtained from Goodfellow Corp. USA.

For preparation of composite electrolytes the CsH₂PO₄ and SiC powders were mixed in an agate mortar with ethanol (3.38 g CsH₂PO₄ and 1,35 g SiC with 3.7 mL ethanol). Two drops of 85% phosphoric acid were added, and the mixture was further mixed by using a mortar and pestle until a viscous paste/slurry was obtained. A disk of PBI felt having a diameter corresponding to the finished electrolyte (42 mm) was wetted with an ethanol-phosphoric acid mixture for at least 1 hour, before it was immersed into the slurry. In some cases the disk covered with slurry was further ultra sonicated for 20 minutes. Then the disk was placed on top of a disk of a protection Teflon foil also having a diameter of 42 mm, and the excess phosphate slurry was distributed over its surface and allowed to dry. The disk with the Teflon disk was transferred to a custom made 42 mm diameter pellet pressing tool. A second disk of Teflon foil was placed on top of the disks, and finally a steel piston/disk was added as the upper part of the pressing tool. The pressing tool was placed in a hot pressing device allowing the tool to be heated up to 160 °C. The electrolyte was pressed at 2000 kg force for 60 minutes at 160 °C. The tool was allowed to cool to room temperature before opening and separating the protection Teflon disks from the electrolyte. The thicknesses of the prepared electrolytes were typically around 1.0 mm (not all slurry was used). A typical weight of the pressed electrolyte was 3.6 g out of 4.7 g of initial chemicals.

It was observed that an apparent density of at least 2.5 g/cm³ was required to make a gas tight electrolyte. Characterization of the electrolyte materials by XRD for phase composition - before and after testing in electrolyzer - was done using a Rigaku Miniflex 600 instrument with a CuKα X-ray source.

Electrodes:

Nickel powder (obtained from Alfa Aesar, Thermo Fischer, USA) with particle sizes of 3-7 µm and a purity of 99.9 % was used. The porous Ni-cathodes were prepared by pressing pellets of nickel powder at 1600 kg/cm². Their thickness was 1.1 mm and their diameter was 30 mm. The porosities of the electrodes were determined from weighing and the geometrical dimensions and were ~42 % by volume.

Anodes were prepared as follows: Stainless steel felt from JL-Fiber Science and Technology Co., Ltd. (China). They were built of two layers, one layer having a fiber diameter of 8 μm , and another one having a fiber diameter of 12 μm . Each layer was coated with a tight layer of tantalum metal by a chemical vapor deposition process developed by Tantaline A/S (Denmark). The optimal thickness of the tantalum coating was around 5 μm . The porosity of the coated felt was estimated to be ~45 %.³⁰

Discs of the desired diameter, 30 mm, were stamped out by a hydraulic stamping machine, and an ink of IrO₂ and PBI in formic acid was sprayed onto the surface of the layer containing the 8 μm thick fibers that were kept at ca. 140 °C (causing instant drying). The applied loadings were approximately 4.5 mg/cm² IrO₂ and 0.5 mg/cm² PBI.

Results and discussion

A number of test experiments were done with different electrodes and conditions. In each experiment the composition of the outlet gas from the electrolyser was analyzed by gas chromatography and reported for their different current densities, as shown in Fig. 2. It can be seen that the carbon dioxide signal is very large compared to the signals from the other components. This is to be expected since the carrier gas is used in large excess. The main product is CH₄, with H₂ as the second most important product found. Nitrogen can enter the pressurized system via the surrounding autoclave atmosphere through small leaks, or it may enter the unpressurised section between the autoclave and the gas chromatograph from the air. The oxygen on the other hand, besides coming from the air, may penetrate into the cathode product gas from the anode chamber of the cell. This may happen because the sealing by the Kapton/Papyex gaskets at the edge of the electrolyte may not be working perfectly, or because the electrolyte might not be completely gas tight and a pressure difference might have formed during operation between the electrode chambers. It can be seen that the amount of oxygen to the amount of nitrogen, is larger than the standard 21% in air. Therefore some of the oxygen present must have passed through the sealing or through the electrolyte itself from the anode chamber to the cathode outlet.

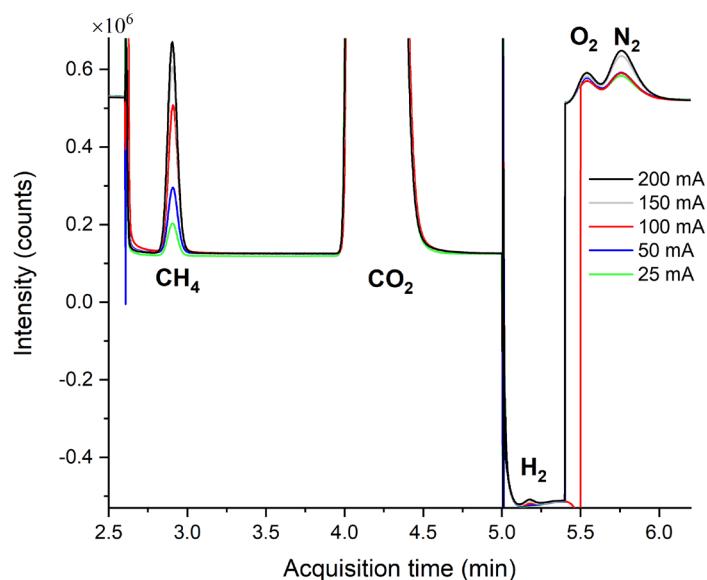
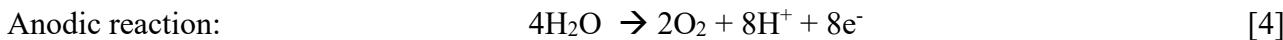


Figure 2. Gas chromatography result of the reaction products from electrolysis at different currents. Conditions: Nickel cathode, 30 mm in diameter (7.07 cm^2) at 300°C and ~ 8 bar. Electrolyte: ~ 3.38 g CsH_2PO_4 , ~ 1.35 g SiC and ~ 0.2 g H_3PO_4 . Anode: size 7.07 cm^2 , $4.5 \text{ mg/cm}^2 \text{ IrO}_2$ and $0.5 \text{ mg/cm}^2 \text{ PBI}$. Gas flows at the outlet of the reactant gases (1bar and ambient temperature): 20 mL/min CO_2 , $13 \text{ mL/min H}_2\text{O}$.

We know from electrochemical experiments in molten CsH_2PO_4 at 350°C that CH_4 is formed not by a chemical reaction with H_2 but by an electrochemical process that we have named co-electrolysis.²⁹ The required potential to make the current pass is so low that it is clear that the reaction cannot just be formation of hydrogen that subsequently reacts with CO_2 to make the methane. Since the condition in the present system is not far from the conditions described in Ref. 29 our best explanation for the formation of methane is according to the following reactions (H^\cdot denotes an atomic hydrogen radical sitting on the cathode>):



It can be seen that 4 mol of water are consumed at the anode and 2 mol are produced at the cathode. Some of the cathode water may actually diffuse to anode reducing the need for water there. Simultaneously one mol of CO_2 is consumed and one mol of CH_4 is formed at the cathode.

Fig. 3 shows a polarization curve obtained by consecutive runs at constant current until stabilization of the voltage was obtained for each level of current, typically after 400-500 seconds. For low currents (about 5 mA/cm^2), electrolysis starts at ca. 1.10 V , remarkably close to the thermodynamic values of water splitting as well as of the direct co-reduction of CO_2 and H_2O at 1.06 and 1.01 V , respectively. However, the curve is approximately linear and the voltage rises quickly with

increasing current, indicating either a large ohmic resistance in the cell or a large polarization resistance on one or both electrodes. The latter may be due to the phenomenon that only a limited amount of catalyst material is active in the electrodes due to non-optimized electrode structure.

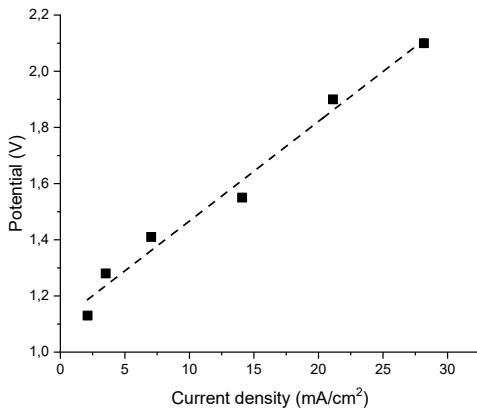


Figure 3. Polarization curve with nickel cathode (30 mm in diameter or 7.07 cm^2) at 300°C and ~8 bar. Electrolyte: ~3.38 g CsH_2PO_4 , ~1.35 g SiC and ~0.2 g H_3PO_4 . Anode: $4.5 \text{ mg}/\text{cm}^2$ IrO_2 and $0.5 \text{ mg}/\text{cm}^2$ PBI.

The impedance measurements in Fig. 4 show that the ohmic resistance of the electrolyte is only 1.24 Ohm (Fig. 4), which will cause a voltage increase of only 0.033 V when the current density was increased from 0 to $27 \text{ mA}/\text{cm}^2$. As it can be seen from Fig. 3 the voltage rises much faster than that, ca. 1 V for the same range, and it must therefore be concluded that only a minor part of the increase arises from the ohmic resistance of the electrolyte, and consequently only a smaller part of the electrodes is utilized; hence it is not the electrolyte that is causing the voltage increase. It should be noted that we have also made the gas channels broader than necessary to avoid clogging, and in this way we may have reduced the active area of the electrodes. From other experiments we know that the size of the channels and the structure of the electrodes are important for the results.

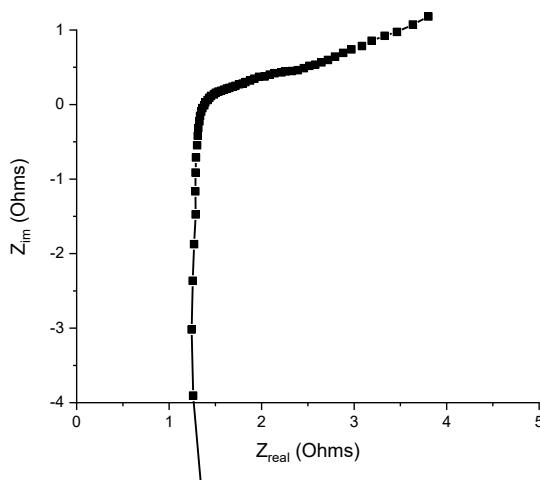


Figure 4. Impedance measurements showing a resistance of 1.24 Ohm of the electrolyte. Conditions: Nickel cathode (30 mm in diameter or 7.07 cm^2) at 300°C and ~8 bar. Electrolyte: ~3.38 g CsH_2PO_4 , ~1.35 g SiC and ~0.2 g H_3PO_4 . Anode: $4.5 \text{ mg}/\text{cm}^2$ IrO_2 and $0.5 \text{ mg}/\text{cm}^2$ PBI.

The rates of product formation for the various current densities were quantified by integration of the peaks in the gas chromatograms for methane and hydrogen. From the areas obtained, the content of H₂ and CH₄ in the gas mixture was determined by the use of standard curves for the compounds. Figs. 5 and 6 show the signal peaks rising for CH₄ and H₂, respectively, as functions of the applied with increasing current densities.

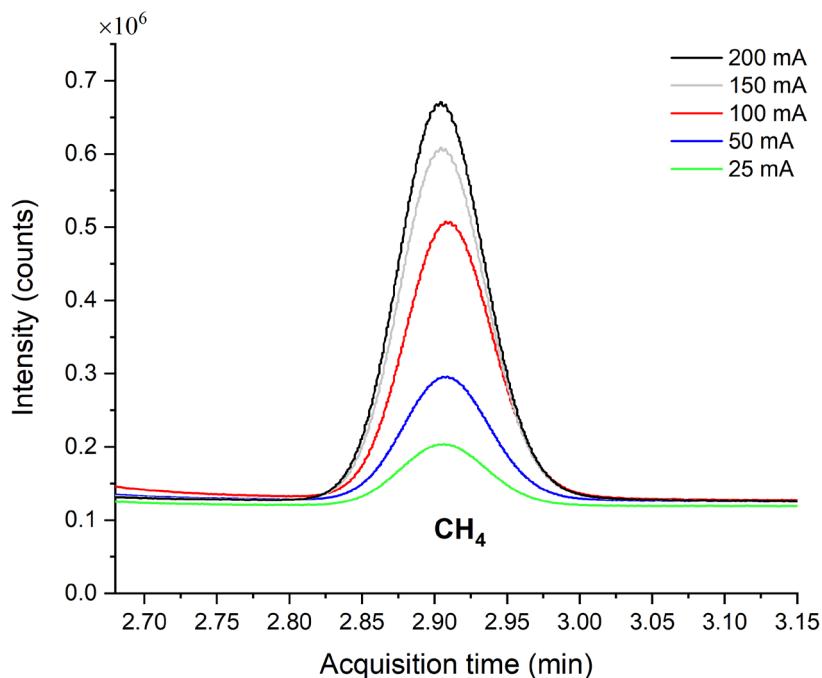


Figure 5. Gas chromatograms of the CH₄ peak at different currents. Nickel cathode (30 mm in diameter or 7.07 cm²) at 300 °C and ~8 bar. Electrolyte: ~3.38 g CsH₂PO₄, ~1.35 g SiC and ~0.2 g H₃PO₄. Anode: 4.5 mg/cm² IrO₂ and 0.5 mg/cm² PBI. Gas flows at the outlet of the reactant gases and CH₄ (1bar and ambient temperature): CO₂: 20 mL/min, H₂O: 13 mL/min, CH₄: 0.038, 0.081, 0.183, 0.232, 0.263 mL/min (in the interval 25—200 mA).

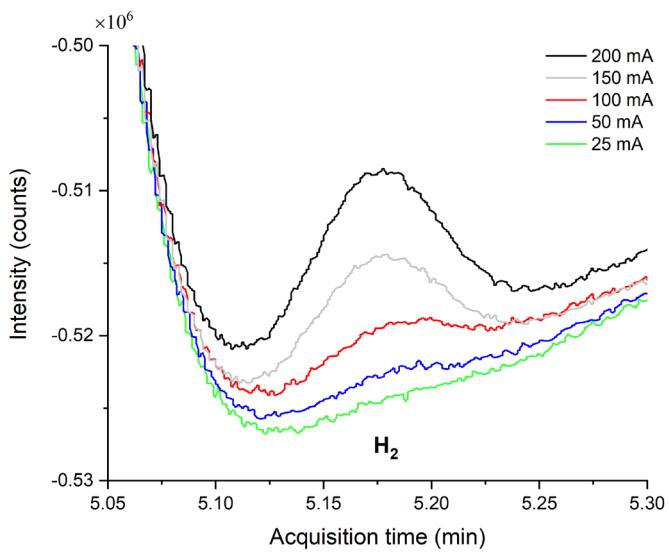


Figure 6. Gas chromatograms of the H_2 peak at different currents. Conditions: Nickel cathode (30 mm in diameter or 7.07 cm^2) at 300°C and ~8 bar. Electrolyte: ~3.38 g CsH_2PO_4 , ~1.35 g SiC and ~0.2 g H_3PO_4 . Anode: $4.5 \text{ mg/cm}^2 \text{IrO}_2$ and $0.5 \text{ mg/cm}^2 \text{PBI}$. Gas flows at the outlet of the reactant gases and H_2 (1 bar and ambient temperature) CO_2 : 20 mL/min, H_2O : 13 mL/min, H_2 : 0.000, 0.001, 0.030, 0.081, 0.132 mL/min (in the interval 25—200 mA).

In Fig. 7 the amounts of CH_4 and H_2 in the outlet gas are compared with the amount of charge passed. It is clear from the figure that the total faradaic efficiency for methane is close to 100% in the range of 10–15 mA/cm² and the selectivity for CH_4 is decreasing with increasing current density. This is not a surprise if one looks at the electrode reactions (Eqs. 1 – 4). If there is **not** enough CO_2 available which will happen at higher current densities two H^- will tend to form one H_2 . It can also be seen that the combined efficiencies do not add up to 100%. A likely explanation could be some leaking of the gases.

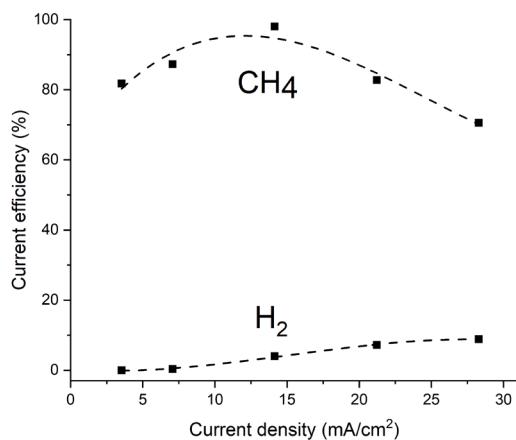


Figure 7. The Faraday efficiencies for formation of CH₄ and H₂ with polynomial fits of 3rd order (cubic functions). Conditions: Nickel cathode (30 mm in diameter or 7.07 cm²) at 300 °C and ~8 bar. Electrolyte: ~3.38 g CsH₂PO₄, ~1.35 g SiC and ~0.2 g H₃PO₄. Anode: 4.5 mg/cm² IrO₂ and 0.5 mg/cm² PBI. Gas flows at the outlet (1bar and ambient temperature): CO₂: 20 mL/min, H₂O: 13 mL/min.

The experiments until now have only been running for a day at a time and it is difficult to restart an experiment after the cell has been cooled down. A problem was also to adjust the amount of electrolyte to the support. In case of too much electrolyte the electrodes will be floating, and if too little the compartment will not be gastight.

Conclusions

It has been shown that by co-electrolysis of CO₂ and H₂O it is possible to produce methane with H₂O and a little H₂ as the only reaction products, when using CsH₂PO₄ as electrolyte, a nickel cathode, an IrO₂ anode, a temperature of 300 °C and a pressure of ~8 bar. The current density for the maximum selectivity of methane (close to 100%) was in the range 10 – 15 mA/cm². At higher current densities decreasing efficiencies were observed. The restriction here was probably due to difficulties in getting enough CO₂ to the cathode. This is a problem which could be improved by changing the design of the electrolysis cell or raising the CO₂ pressure. Another thing is the long-time stability of the experimental setup which has not been examined in details yet. We know however that the performance of our setup decreases during the run of a day. We think this decrease is due to loss of the electrolyte into the porous electrodes. We are working to develop better ways to keep the electrolyte in its right place.

Acknowledgments

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References

1. Y. Hori, K. Kikuchi and S. Suzuki, *Chem. Lett.*, **11**, 1695 (1985).
2. K. P. Kuhl, E. R. Cave and D. N. Abram and T. F. Jaramillo, *Energy. Environ. Sci.*, **5**, 7050 (2012).
3. R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo and M. T. M. Koper, *J. Phys. Chem. Letters*, **6**, 4073 (2015).
4. Y. Hori, A. Murata, R. Takahashi and S. Suzuki, *J. Am. Chem. Soc.*, **109**, 5022 (1987).
5. K. Hara, A. Kudo, T. Sakata and M. Watanabe, *J. Electrochem. Soc.*, **142**, L57 (1995).
6. S. D. Ebbesen, S. H. Jensen, A. Hauch and M. B. Mogensen, *Chem. Rev.*, **114**, 10697 (2014).
7. T. L. Skafte, P. Blennow, J. Hjelm and C. Graves, *J. Power Sources*, **373**, 54 (2018).
8. K. Xie, Y. Zhang, G. Meng and J. T. S. Irvine, *J. Mater. Chem.*, **21**, 195 (2011).
9. E. Erdle, W. Dönitz, R. Schamm and A. Koch, *Int. J. Hydrogen Energy*, **17**, 817 (1992).
10. M. Rodier, Qingfeng Li, R. W. Berg and N. J. Bjerrum, *Appl. Spectrosc.*, **70**, 1186 (2016).
11. A. V. Nikiforov, I. M. Petrushina, E. Christensen, N. V. Alexeev, V. A. Samokhin and N. J. Bjerrum, *Int. J. Hydrogen Energy*, **37**, 18591 (2012).
12. A. V. Nikiforov, R. W. Berg, I. M. Petrushina and N. J. Bjerrum, *Applied Energy*, **175**, 545 (2016).
13. R. W. Berg, A. V. Nikiforov, I. M. Petrushina and N. J. Bjerrum, *Applied Energy*, **180**, 269 (2016).
14. A. V. Nikiforov, R. W. Berg and N. J. Bjerrum, *Ionics*, **24**, 2761 (2018).
15. R. W. Berg, A. V. Nikiforov and N. J. Bjerrum, *J. Phys. Chem. Solids*, **136**, 109177 (2020).
16. D. A. Boysen, T. Uda, C. R. I. Chrisholm and S. M. Haile, *Science*, **303**, 68 (2004).
17. J. Otomo, T. Tamaki, S. Nishida, S. Wang, M. Ogura, T. Kobayashi, C-J. Wen, H. Nagamota and H. Takahashi, *J. Appl. Electrochemistry*, **35**, 865 (2005).
18. T. Matsui, T. Kukino, R. Kikuchi, and K. Eguchi, *J. Electrochem. Soc.*, **153**(2), A339 (2006).
19. P. Bocchetta, R. Ferraro, and F. Di Quarto, *J. Power Sources*, **187**, 49 (2009).
20. A. H. Jensen, Q. Li, E. Christensen and N. J. Bjerrum, *J. Electrochem. Soc.*, **161**, F72 (2014).
21. J. Otomo, N. Minagawa, C. Wen, K. Eguchi and H. Takahashi, *Solid State Ionics*, **156**, 357 (2003).
22. V. G. Ponomareva and E. S. Shutova, *Russ. J. Electrochem.*, **43**, 521 (2007).
23. S. Oh, E. K. Insani, V. H. Nguyen, G. Kawamura, H. Muto, M. Sakai and A. Matsuda, *Sci. Technol. Adv. Mater.*, **12**, 034402 (2011).
24. G. V. Lavrova, E. S. Shutova, V. G. Ponomareva and L. A. Dunyushkina, *Russ. J. Electrochem.*, **49**, 718 (2013).
25. T. Anfimova, A. H. Jensen, E. Christensen, J. O. Jensen, N. J. Bjerrum and Q. Li, *J. Electrochem. Soc.*, **162**, F436 (2015).
26. Unpublished results.
27. J. Ribeiro and A. R. De Andrade, *J. Electrochem. Soc.*, **151**, D106 (2004)
28. N. J. Bjerrum, I. M. Petrouchina, A. Nikiforov and R. W. Berg, Patent International Publication Number WO2019/048016 A1 (2019).
29. A. V. Nikiforov, I. M. Petrushina, E. Christensen, R. W. Berg and N. J. Bjerrum, *Renewable Energy*, **145**, 508 (2020).
30. M. K. Hansen, “PEM Water Electrolysis at Elevated Temperatures”, Ph.D. Thesis, Technical University of Denmark (2012).