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Voltammetric study of one-step electrochemical methane production during water and CO₂ co-electrolysis in molten CsH₂PO₄

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ABSTRACT

Cyclic voltammetry was performed with a nickel electrode in molten CsH₂PO₄ at 350 °C and at approximately 25 bar of water pressure. The effect of adding carbon dioxide was examined. It is found that even small amounts of CO₂ (partial pressure below 0.2 bar at 350 °C, corresponding to 0.5 bar at 22 °C of a 5:1 mixture of N₂:CO₂) have a pronounced effect on the cyclic voltammetry curves. Under these conditions the hydrogen formation is substituted by another process, methane formation. At the same time the cathodic current increased by a factor of 4-6, meaning that the ease of methanisation was much improved.

Keywords:

Co-electrolysis

Carbon dioxide

CsH₂PO₄

Methane

Voltammetry

1. Introduction

One way of storing electrical energy is to split water into hydrogen and oxygen by electrolysis via reaction (1). The products of such water electrolysis contain chemically free energy (standard free energy of formation, $\Delta_f G^\circ$) bound as hydrogen and oxygen.

Hydrogen, as a fuel product, is satisfactory for the small-scale fuel production, e.g. at hydrogen refueling stations for fuel cell cars. However for mass production scale, methane will be more useful for energy storage instead of hydrogen, because (i) the energy content by volume of hydrogen is lower than for methane and because (ii) methane can be introduced directly into existing methane gas networks. The standard heat of combustion of one mol of H_2 to H_2O gas at 25 °C and 1 bar (STP), is $\Delta_c H^\circ = -241.826 \text{ kJ/mol}$ whereas the heat of combustion of one mol of CH_4 to gasses at STP is $\Delta_c H^\circ = -802.301 \text{ kJ/mol}$ according to calculations using the values of Chase et al. [1].

There are two possible ways of storing energy using the method of water electrolysis with methane as the final product.

The first way includes commercial water electrolysis, reaction (1), as a first step, and reacting the electrochemically produced hydrogen with CO_2 through the Sabatier reaction as a second step followed by condensation of the water, reaction (2) :

The second way, which is under development now in various laboratories [2]-[4], involves CO_2 – water co-electrolysis as a first step involving solid oxide electrolysis cells (SOEC), using yttria-stabilized zirconia as electrolyte, with syngas ($\text{CO} + \text{H}_2$) as cathodic products and with O_2 as an anodic product, reaction (3).

A second step, the Fischer-Tropsch process, is then performed with more hydrogen and followed by condensation of the water, reaction (4) :

The present paper describes the result of our research in a similar field of research: Intermediate temperature direct electrolysis [5]-[7]. In a recent study we have shown that CsH_2PO_4 can be used as an electrolyte, and with Nickel as the cathode material and in the presence of CO_2 we can obtain methane as a cathodic product of the electrolysis, at temperatures up to 350°C and at water vapor pressures of up to 25 bar [8]. The reason for choosing Ni as the cathode has been that nickel is known to enhance the formation of methane in the Sabatier process [9],[10].

Whereas there have been several attempts to use CsH_2PO_4 as the electrolyte in intermediate temperature fuel cells [11]-[17], only few attempts have been made on water electrolysis and none under pressurized conditions and in the presence of CO_2 . Containment is needed to confine the water into the melt because otherwise the high conductivity of the electrolyte will be lost due to reaction (5):

that is leading to loss of water as vapor and formation of solid or dissolved CsPO_3 with low conductivity because of lack of hydrogen ions that can carry the charge during electrolysis, compared to the situation in molten CsH_2PO_4 [7].

In a recent study the best experimental fuel cell results so far [18] were obtained in a $\text{Pt/CsH}_2\text{PO}_4/\text{IrO}_2$ system at 265°C by using current densities of -20 mA/cm^2 at potentials of 1.9 V. This use of expensive materials were applied to make the cell work. The CsH_2PO_4 electrolyte was not recommended for water electrolysis because of the high voltage needed at the relative low temperatures used until now.

Solid CsH_2PO_4 has been used as electrolyte in CO_2 water co-electrolysis at $200-300^\circ\text{C}$ [19]. The main conclusion was that there was no evidence for electrochemical reduction of CO_2 on the Cu-based cathodes used in that investigation.

The aim of this paper was to study instead the electrochemical behavior of CO₂ on a Ni cathode at higher temperatures and the dependence on the partial pressure of carbon dioxide during such an electrolysis. The processes that we estimate to happen can be described by the following reactions:

The overall or net reaction is referred here to as a one-step reaction because it seems to behave like that and the details of the path are not known.

2. Experimental

2.1. Fabrication of quartz cells

We needed to develop cells designed to study our system. The cells were fabricated in our glass workshop to investigate the electrochemical behavior of nickel-coated electrodes in molten CsH₂PO₄ (CDP) solution. Nickel was thought to be ideal for the reaction. The problem is the high water pressure that is necessary to prevent the CDP from decomposing, e.g. about 25 bar at ~350 °C [6],[7], which demands a completely closed system, provided with tight electrical lead-ins. A suitable cell (Fig. 1) was therefore constructed from fused quartz glass. At first, two bulbs of a standard halogen lamp (PHILIPS type 7787XHP 36 V/400 W) were cut near the base and elongated to produce a two chamber cell, separated by an 8 mm in diameter quartz filter (E, Fig. 1) having the designation “Por.3”, or “P16”, i.e. having pore sizes in the range of 16-40 microns, international standard ISO 4793-80. A pressure equilibrating bridge (D, Fig. 1) was added, approximately 30 mm above the electrodes. Spirals (diameter 0.3 mm) inside the chambers were obtained in the following manner: a spiral in the chamber to be used as a reference electrode (F, Fig. 1) was left as originally produced (total length approximately 210 mm). One of the windings of the spiral in the other chamber was cut in two in order to leave a single pin useful as a working electrode (length approximately 14 mm, B, Fig. 1). The rest of the 15 ± 1 windings on the other pin formed a counter electrode (length approximately 185 mm, A, Fig. 1).

Figure 1. The type of cell used in all experiments before it was filled with chemicals and sealed off. A: Platinum coated counter electrode. B: Nickel coated working electrode. C: Light bulb electrical lead-ins. D: Pressure equilibration bridge. E: Porous membrane. F: Silver coated reference electrode.

Cells delivered from the glassblower were cleaned, etching off the WO_3 (formed on the electrodes during the glass blowing) by means of filling the whole cell with an equimolar mixture of solid $\text{K}_2\text{S}_2\text{O}_7$ and K_2SO_4 salts and heating it in the open to get a melt at approximately 300-440 °C by means of a butane-oxygen flame. Details of the dissolution process have been given previously [5], [20]. After that the cells were washed by flushing with hot tap water to dissolve the salts, followed by repeated rinsing with ultrapure water (resistivity = 18 M Ω cm) in an ultrasonic bath. Finally, the cells were dried in a heating cabinet at 80 °C.

2.2. Coating of the electrodes

The tungsten electrodes needed further cleaning in order to make it possible to obtain tight metal coating layers by electrochemical deposition. The following procedure was used in all the experiments: The electrodes in the cells were covered with 10 wt. % sulfuric acid. A reducing current was applied, using a platinized Ti counter electrode provided by Elplatek A/S (Denmark). The current density was $\sim 1.5 \text{ A/cm}^2$ for the working electrode and $\sim 0.3 \text{ A/cm}^2$ for the counter and reference electrodes. The duration of these procedures was ~ 90 seconds in all cases. Then the cells were washed several times with ultrapure water in an ultrasonic bath and dried.

After that, electrocoating of the electrodes was performed using galvanic baths with the following concentrations: Platinum: 2 g of Pt /L (pH <1, Platuna N1) and gold: 4 g of Au /L, both provided by Elplatek A/S. The *counter electrode* was first coated with a strike layer of gold [21], done with a current density of 10 mA/cm^2 for 20 minutes followed by a layer of platinum [22] with a current density of 20 mA/cm^2 for 40 minutes. For the *reference electrode* the strike coating was obtained by first applying a solution made primarily from potassium cyanide with a little potassium silver cyanide, and using a current density of 30 mA/cm^2 for 2 minutes. Then a new mixture was applied, similar to the one already used but with a further addition of Bright Silver ELFIT 73 [23], and with a current density of 10 mA/cm^2 for 15 minutes in order to obtain a massive layer of silver.

At last the *working electrode* was coated with metallic nickel [24] by using a nickel strike bath with a concentration of 18 g/L in 120 ml/L HCl. The strike coating was added at room temperature, applying a current density of 54 mA/cm^2 for 1 minute. Then the second Ni layer was deposited at ca. 65°C [24]. The current density was changed to 38 mA/cm^2 applied for 60 minutes, using a Super-Bright Nickel Slotonik 40 bath. The temperature was maintained ($\pm 5^\circ\text{C}$) by blowing hot air onto the cell with a heat gun and, while the temperature of the coating solution inside the cell was measured with a k-type thermocouple, covered with Teflon[®] PTFE (Omega Co.) and inserted into the working cell.

Between and after performing the coating of the electrodes with different metals the cells were repeatedly washed with ultrapure water, and finally the cells were dried in a heating cabinet at 80°C and kept under vacuum ($< 0.1 \text{ Torr}$) for at least 10 minutes to assure cells were completely dry and did not contain any traces of water.

2.3. Verification of coatings

In order to make sure that we had the right coatings a series of experiments were performed to check that the whole tungsten spiral wire was coated with either Pt, Ni or Ag on the outside. Cross-

sections of the tungsten spiral wire samples with and without coatings were examined by scanning electron microscopy (SEM) and energy dispersive X-ray diffraction (EDX) on samples mounted in PolyFast phenolic hot mounting resin with carbon filler (provided by Struers A/S, Denmark). SEM measurements were made with an EVO 10 scanning electron microscope. The identities of the metal coatings were verified by EDX on an INCA-system from Oxford Instruments, operated with an accelerating voltage of 20 kV and a working distance (WD) of 8 mm. Inspections of the cross section coatings are given in Figs. 2 and 3.

Figure 2. Scanning electron microscope cross sections of samples of an uncoated 0.3 mm nominally thick W wire (left) and a platinum coated W wire like the ones used for the counter electrodes (right). The identities of the metals were confirmed by EDX. The $\sim 30 \mu\text{m}$ thick platinum coating appeared to be tight, although containing cracks. Internal darker traces of grinding are seen. Spots are artefacts due to micro-crystallinity.

Figure 3. Scanning electron microscope cross sections of a 0.3 mm W wire coated with Ag like the ones used for reference electrodes (left) and a similar Ni coated working electrode (right) as seen by magnification. The metals were identified with electron diffraction in the microscope. The coatings appeared rather tight.

2.4. Filling and sealing of the cells

The cells were filled with enough CDP crystallites in the working electrode chamber such that the salt after melting should cover 80-90% of the working electrode surface. The reference electrode chamber was filled by a mixture of Ag_3PO_4 and CsH_2PO_4 in mole ratio 1 to 9 in the way that Ag_3PO_4 was added at first, followed by addition of CDP. The CsH_2PO_4 was prepared as described elsewhere [7]. Ag_3PO_4 was prepared by adding AgNO_3 to an aqueous solution of Na_3PO_4 in a molar ratio of 3 Ag to 1 P to obtain a yellow precipitate, and then isolating and repeated washing it with ultrapure water on a filter connected to a vacuum pump. Finally, after filtration and repeated washing the Ag_3PO_4 was fully dried in darkness (in a furnace at 80 °C for several hours). After evacuation to < 0.1 Torr, the cell was connected to a vacuum line and filled with either of the investigated gases or mixtures (carbon dioxide and/or nitrogen), added up to a total pressure of 0.5 bar at ~22 °C (the pressure was read off on a calibrated Bourdon manometer). Finally the cell was sealed off with a butane-oxygen torch flame. The gas mixtures were prepared beforehand by mixing gases delivered in 50 L bottles, from AGA A/S, Denmark, namely CO_2 UN1013 and *instrument* N_2 5.0 UN1066. A setup allowed us to mix gases from large 50 L bottles in a smaller empty gas bottle, filling it up to a partial pressure of 3 bar of each gas at room temperature. The gas mixtures in the smaller bottles were homogenized over night by use of a rolling table.

2.5. Electrochemical experiments

Cyclic voltammetry (CV) was used in this investigation in order to study the electrochemical behavior of the nickel electrode under the various conditions. Each cell was at first heated up to 250 °C with terminals connected and no potential supplied. Then the heating was continued with a slightly negative potential (-0.001 V) of the Ni working electrode vs. the Ag/ Ag_3PO_4 reference electrode, and the cell equilibrated for several hours at a temperature of ~350 °C. During the CV measurements, the potential of the Ni working electrode was linearly changed with time from ~0 V to -1.0 V (vs. the reference electrode), using 500 and 50 mV/s as potential sweep rates. The current mainly runs between the Ni working and the Pt counter electrodes and the measurements are

presented as conventional current-potential plots, see Figs. 4 and 5. On these plots, each peak or sudden increase of current during scanning must be due to movements of electric charges, i.e. electrochemical reactions. At the end of the experiments one cell exploded because of the high internal pressure in the cells; the replacement cell gave identical curves, indicating the reproducibility of the experiments.

3. Results and discussion

Results were obtained for nickel electrodes in molten CsH_2PO_4 in four cells under different gaseous atmospheres: pure N_2 , $\text{N}_2:\text{CO}_2 = 5:1$, $\text{N}_2:\text{CO}_2 = 1:1$ and pure CO_2 as given in Figs. 4 and 5, respectively for two different potential scan rates (500 mV/s, fast and 50 mV/s, slow). By comparing these four different cells, we can make several important observations.

The curves start from 0.0 V vs. the $\text{Ag}/\text{Ag}_3\text{PO}_4$ reference electrode (right side of the diagram, running to the left). In the beginning, the current density is positive corresponding to some *oxidation* process on the working electrode, presumably involving formation of Ni^{2+} compounds. At some potential of the working Ni electrode, at around -0.7 ± 0.2 V (potentials are given vs. the $\text{Ag}/\text{Ag}_3\text{PO}_4$ reference electrode in the following discussion), the current density changes to negative values (reversal of current direction) and *reduction* processes start at the Ni electrode (see in the left side of Figs 4 and 5). When scanning back from -1 V (i.e. reversing the supplied potential scanning direction) the reduction speeds are at first decreasing, and when the current density becomes positive, oxidation processes restart.

Nitrogen. For the Ni electrode in *pure nitrogen* atmosphere, it can be seen that there is a very low electrochemical activity, i.e. only small currents occur (red curves, positive and negative current densities) when no CO_2 is present. We note that a weak anodic current presumably forming Ni^{2+} runs until a cathodic reaction (reduction) starts at around -0.8 to -0.9 V (vs. the $\text{Ag}/\text{Ag}_3\text{PO}_4$ reference electrode). Presumably it is the reduction of previously formed Ni^{2+} or it could be protons from water or $\text{H}_2\text{PO}_4^{2-}$ groups in the electrolyte that are forming hydrogen according the reaction (1). What else could it be? Reduction of Cs^+ and P^{5+} is not likely at those potentials. It cannot be reduction of N_2 because the blue points for the pure CO_2 curves correspond to the cell *without* N_2 (pure CO_2) and these points remind of the green curves for experiments that *do contain* N_2 . When scanning back from -1 V, the reduction speed levels off (H_2 formed at slower speed) and oxidations (anodic reactions) start at positive current densities in the upper right half of the Figs. 4 and 5, presumably being due to formation of Ni^{2+} compounds again (red open circles).

Cells with CO₂. The effects of addition of *more and more* CO₂ on to the electrochemical cells at the expense of the nitrogen and the resulting behavior of the protons in the molten CsH₂PO₄ are studied in the following (results shown as the *black, green and blue* curves in Figs. 4 and 5). In each figure the traces of the curves change in response to the increasing content of CO₂ in the gas (added at the expense of N₂; the total pressure is kept at ~1 bar at 350 °C). We note the following changes (see the lower left corner of the Figs. 4 and 5, for negative currents densities): The cathodic currents increase from about -150 to about -700 mA/cm², i.e. by ~4 to ~6 times. The only reason for this to have happened must be the presence of the CO₂. The current density (speed of reduction process) is now quite large corresponding to a realizable reduction reaction. The most obvious one is the formation of methane according to reaction (8).

The backward scan curves (from potentials of -1 V towards 0 V) exhibit decreasing reduction currents until oxidation waves (positive current densities) start to occur at potentials vs. Ag/Ag₃PO₄ higher than about -0.8 to -0.7 V. The *oxidation* waves in the backward scan curves exhibit maxima at about -0.5 V (Fig. 4) or at about -0.65 V (Fig. 5) vs. the Ag/Ag₃PO₄ reference electrode.

This behavior is a sign of the above mentioned so-called *one-step* or direct electrochemical-chemical (EC) mechanism of the electrolysis (reaction 8). In the studied cells containing CDP, the electrochemical steps are interpreted to involve the formation of hydrogen by the *Cathodic reduction*, reaction (6) simultaneously with or preceeded or followed by another *Chemical step*, reaction (7), such that totally the *Net Reaction* (8) proceeds forming methane. This overall methane formation has already been confirmed by gas chromatographic and Raman measurements [8]. From the cell with N₂:CO₂ = 5:1 that survived cooling down from the high temperature voltammetry experiments, a Raman spectrum of the gas at room temperature showed the presence of the methane formed directly, see the methane ν_1 band at 2917 cm⁻¹ in Figure 6. No traces of formed hydrogen or oxygen were seen, probably because of a back reaction on the platinum electrode.

Such a direct electrochemical-chemical or one-step methanisation reaction occurs when some part of the reactants (here the products 2 H₂O) of the chemical step, reaction (7) constitutes part of the reactants in another (preceeding or following) electrochemical step, (reaction (6)). The 2 molecules of water is among what is consumed in reation (8) during the formation of methane.

When comparing the blue and green curves in Figs. 4 and 5 it can be seen that there is not much difference between the measurements with ~1 bar of CO₂ at 350 °C (~0.5 bar at room temperature, blue curves) and the measurements with a somewhat diluted CO₂ gas (~0.50 bar partial pressure of CO₂ at 350 °C (from ~0.5 bar at 22 °C of a 1:1 mixture of N₂:CO₂, green curves). On the other hand when comparing the blue curves (neat CO₂) to the measurements with ~0.17 bar of CO₂ at 350 °C (obtained from ~0.5 bar at 22 °C of a 5:1 mixture of N₂:CO₂) we observe a decline in the height of the oxidation wave. This is a very important observation because it means that there is room to control any possible transport problems in connection with a limited solubility of CO₂ in the melt, just by adjusting the partial pressure of CO₂.

Moreover, the opposite anodic wave with the broad peak current at approximately at -0.50 V (Fig. 4) and -0.65 V (Fig. 5), can be assumed to ~~probably~~ be an electrochemical oxidation of some kind. It would be fortunate if it could be methane to methanol [25], [26] according to the reaction (9):

but it could also just be a back reaction to CO₂, reaction (10):

It is interesting that reactions (9) and (10) are both favored at elevated pressures, according to the Le Chatelier principle.

Figure 4. Overview of polarization data of Ni-electrode in CsH_2PO_4 at $\sim 350^\circ\text{C}$ and 25 bar of H_2O pressure plus the gas added as indicated. Scan rate 500 mV/s. Total pressure of N_2 , CO_2 and/or mixed N_2 : CO_2 gas in each cell was 0.5 bar at room temperature (~ 1 bar at $\sim 350^\circ\text{C}$).

Figure 5. Overview of polarization data of Ni-electrode in CsH₂PO₄ at ~350 °C and 25 bar of H₂O pressure plus the gas added as indicated. Scan rate 50 mV/s. Total pressure of N₂, CO₂ and/or mixed N₂:CO₂ gas in each cell was 0.5 bar at room temperature (~1 bar at ~350°C).

Figure 6. Raman spectroscopy was used for analysis of the gas over the Ni-electrode in the cell filled with CsH_2PO_4 and $\text{N}_2:\text{CO}_2$ gas = 5:1. After the voltammetric experiments at $\sim 350^\circ\text{C}$ and ~ 25 bar of H_2O pressure, the cell survived being cooled down to room temperature. The analysis was done as described in reference [7]. The Raman spectra of the gas (not all parts shown) were obtained directly on the unopened cell. The spectra indicated the presence of the added N_2 , CO_2 , in addition to traces of water from the salt, but no hydrogen or oxygen bands. The only change due to the heating and the voltammetric scans was the arrival of the methane bands (most pronounced the ν_1 band at 2917 cm^{-1}) shown here. The methane is formed directly via the one-step reaction (8).

4. Conclusions

Electrolysis experiments have been performed with nickel cathodes in CsH_2PO_4 at 350 °C and with different further gas additions and under an intrinsic water pressure of approximately 25 bar. It has been shown that the CO_2 content of the gas above the melt has a very important influence on the nature of the formed electrolysis products. Even small amounts of CO_2 (partial pressure below 0.2 bar at 350 °C) result in higher reduction currents, corresponding to less resistance of electrolysis. We interpret this as due to the formation of CH_4 instead of the expected H_2 . The electrochemical process can be characterized as a catalytic electrochemical-chemical (EC) mechanism of an electrochemical reaction in one step. Hence it is less energy demanding to perform an electrolysis leading to methane formation. The cathodic current increases with a factor of 4-6 times when CO_2 is present, allowing for methanisation. Also, slow scan anodic wave peaks were found at about -0.7 V versus the Ag reference electrode. The peak probably corresponds to the formation of an oxidation product of methane. If this is methanol according to reaction (9) it is highly interesting, but it could also just be CO_2 , by reaction (10). Experiments to test this are being performed.

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