Oxidative conversion of CH_4 on Ni and Ag electrode-catalysts in molten carbonate fuel cell reactor

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A fuel cell system using molten carbonates of potassium and lithium as electrolyte was applied to the oxidative conversion of methane over Ni and Ag electrodes. A possibility of cogeneration of valuable chemicals, like C_2-hydrocarbons, and electricity in such a system was demonstrated. With CO_3^{2-} ions (oxygen) transported electrochemically, the rate of formation of C_2-hydrocarbons and selectivity for them on the Ag electrode were found to be greater than those with oxygen premixed to the gase phase.

Keywords: Oxidative coupling of methane; molten carbonate fuel cell; silver and nickel electrode-catalysts

1. Introduction

Numerous studies on catalytic oxidative coupling of methane to ethane and ethylene have been reported, and this reaction still evokes great interest [1–3].

High operation temperature of the fuel cell such as molten carbonate fuel cell (873–923 K) and solid oxide fuel cell (1073–1273 K) allows, at least in principle, to use not only hydrogen but also more abundant natural gas (methane) as a fuel. Of course, when employing the latter, researchers faced some great problems, i.e. carbon deposition on the electrode and much lower electrochemical activity of methane as compared to hydrogen. Nevertheless, it has been recently shown for solid oxide fuel cell [1,4–8] that both electricity and valuable chemicals such as C_2-hydrocarbons may be produced as a result of direct electrochemical oxidation of methane. This is indeed of interest for catalysis

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and, generally speaking, presents a new method to perform the reaction of oxidative coupling of methane.

In this paper the oxidation of methane over Ag and Ni electrodes in molten carbonate fuel cell (MCFC) systems is discussed.

2. Experimental

Components of a molten carbonate fuel cell were the porous γ-$LiAlO_2$ matrix impregnated by an eutectic mixture of lithium (38 mol%) and potassium (62 mol%) carbonates, and Ni and Ag electrodes. The electrodes were made by pressing metal powders.

The matrix with the electrolyte was a disk of 35 mm diameter and 3 mm thickness. The electrodes were disks (diameter = 23 mm, thickness = 1 mm) too. They were pressed to the matrix to achieve a close contact. The Ag wire which was pressed to the matrix at the cathode side of the MCFC was used as a reference electrode.

There were two MCFC monocells used in the experiments. For both of them the Ag electrode served as a cathode; the anode was either Ni or Ag electrode. Experiments were carried out at 923 K and ambient pressure.

The mixture of O_2 and CO_2 was fed into the cathodic space with 3 cm^3/s flow rate in all operation modes of the MCFC. Contents of O_2 and CO_2 were 33 and 67 vol%, respectively. When the electric current was passed through the MCFC, there were practically no changes in the oxygen concentration in the cathodic space.

Oxidation of methane on Ag anode was studied in both electrocatalytic and conventional catalytic modes. As for Ni anode, that was done in the electrocatalytic mode only. In all the modes the flow of methane was fed at 0.4 cm^3/s to the anodic compartment of the MCFC. The water content in methane did not exceed 3 vol%. Conversion of methane was not higher than 5% in all the experiments.

The electrocatalytic mode of methane oxidation is shown schematically in fig. 1. Under this mode the methane flow did not contain oxygen. It was fed directly into the reaction zone by passing electric current through the cell. In this case carbonate ions are formed at the cathode in the following reaction:

$$CO_2 + \tfrac{1}{2}O_2 + 2e^- \rightarrow CO_3^{2-} . \tag{1}$$

These ions are then transported to the anode through the molten carbonate electrolyte. On the anode they can either discharge followed by O_2 and CO_2 production or oxidize methane,

$$CO_3^{2-} \rightarrow CO_2 + \tfrac{1}{2}O_2 + 2e^- , \tag{2}$$

$$CH_4 + CO_3^{2-} \rightarrow CO + CO_2 + C_2\text{-hydrocarbons} + 2e^- . \tag{3}$$

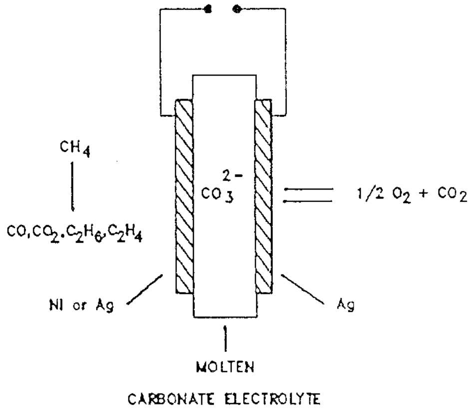

Fig. 1. Schematic diagram of oxidative conversion of methane in the electrocatalytic mode.

When the electric current (I) passes through the cell, the oxygen flow rate (O_f) is calculated from

$$O_f = I/4F, \tag{4}$$

where F is Faraday's constant.

As for the conventional catalytic mode, oxygen was premixed into the methane flow before the latter was fed to the cell. In this case the electric circuit of the cell was open and the anode acted as a regular heterogeneous catalyst.

Compositions of the gas mixture before and after MCFC were analyzed chromatographically. Electric current flowing through the MCFC was controlled by a potentiostat which was employed for measuring the electrode potential as well. The techniques used for the electrochemical and kinetics measurements have been described in detail elsewhere [5].

3. Results and discussion

3.1. EFFECT OF CURRENT ON CELL VOLTAGE AND THE PROBLEM OF THE CARBON DEPOSITION ON ELECTRODES

Current–voltage plots for MCFC using H_2 and CH_4 as a fuel are represented in fig. 2. Note, that the positive values for voltage (V) correspond to the cell operating in the real fuel cell mode, i.e. when the cell generates electricity. At the negative values of V, the cell is supplied with electricity.

As shown in fig. 2, the current–voltage plots for the hydrogen-fueled cells are far above those for the methane-fueled cells. For hydrogen the real fuel cell mode of MCFC operation is achieved over the current range from 0 to 0.7 A for Ni anode (fig. 2a) and from 0 to 0.2 A for Ag anode (fig. 2b). For methane, the real fuel cell mode takes place only within current ranges from 0 to 0.25 A for

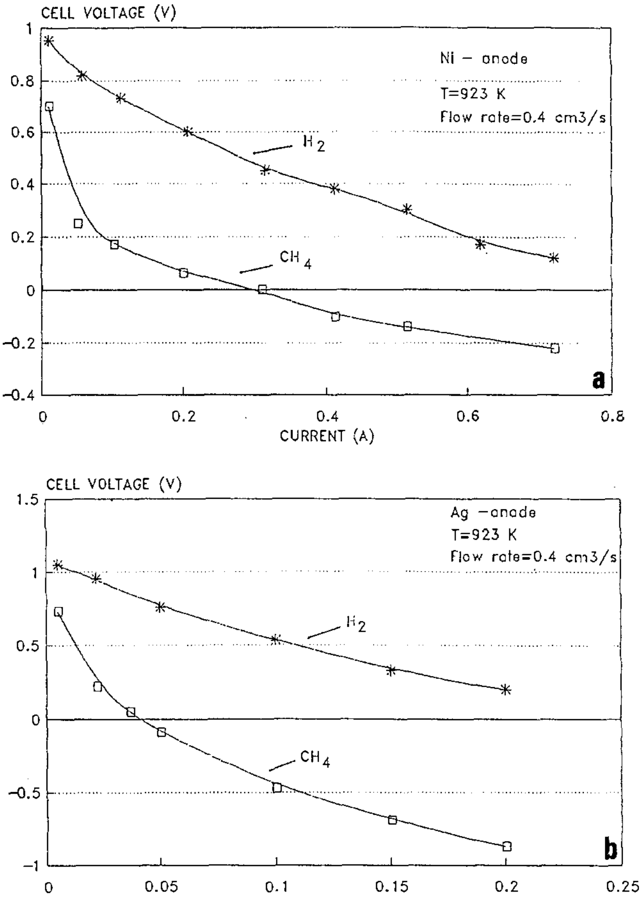

Fig. 2. Current–voltage plots of the MCFC operating with hydrogen and methane. (a) Ni anode and (b) Ag anode.

Ni (fig. 2a) and from 0 to 0.045 A for Ag (fig. 2b). The further increase of the current here becomes possible only in the case of external supplying of electricity into the MCFC systems. These results evidence that the MCFC operating with hydrogen are more efficient than those operating with methane.

The poor performance of the MCFC with methane may be accounted for by not only the inertness of CH_4 molecule itself but also the slight solubility of methane in the electrolyte melt [9] whose film covers an electrode surface. Nevertheless, one can assume that the electrical energy may be produced as a result of the direct electrochemical oxidation of methane on even non-optimized electrodes used in our experiments.

The carbon deposition on the Ag and Ni electrodes was negligible under MCFC operation with methane. This was surprising if the high activity of nickel in CH_4 pyrolysis [10] is taken into consideration. However, the fact that the

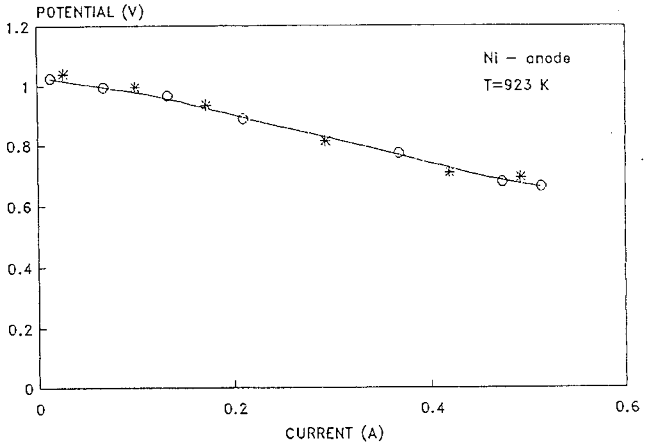

Fig. 3. Effect of current on potential of nickel electrode of hydrogen fueled MCFC. Points (o) and (*) indicate the experimental values recorded before and after 50 h runs of MCFC with methane.

current–voltage plots of the MCFC (fig. 2) remained the same during runs with CH_4 (50 h for Ni electrode and 70 h for Ag electrode) supports this viewpoint. Besides, when measured in hydrogen atmosphere before and after operating the MCFC with methane, the potential of Ni electrode versus current is seen from fig. 3 practically to coincide. This is another evidence that, unlike in the solid oxide fuel cell [6,8], there are no considerable changes in the state of the Ni electrode in the MCFC during electrochemical oxidation of methane. Apparently, the presence of the molten carbonate electrolyte (the melt of an eutectic mixture of lithium and potassium carbonates) on the surface of the electrode inhibits the carbon deposition on the electrode.

3.2. OXIDATIVE CONVERSIONS OF METHANE

When the oxidation of CH_4 is performed in the MCFC systems, the formation of CO_2, H_2O and C_2-hydrocarbons (ethane and ethylene) was observed. Now let us discuss the results obtained.

Fig. 4 shows the effect of current passing through MCFC (oxygen flow through the electrolyte, see eq. (4)) on the steady-state rates and selectivities for the formation of C_2-hydrocarbons upon CH_4 oxidation on Ni and Ag electrodes in the electrocatalytic mode.

It can be seen (fig. 4a) that the rates of the formation of ethane and ethylene on Ni electrode increase with the increase of current. The rate of the formation of C_2H_6 is about 6 times that of C_2H_4. The selectivity for C_2-hydrocarbons, according to the data in fig. 4a, remained almost unchanged and equaled to $\approx 10\%$.

On the Ag electrode (fig. 4b) the rate of the formation of ethane increases

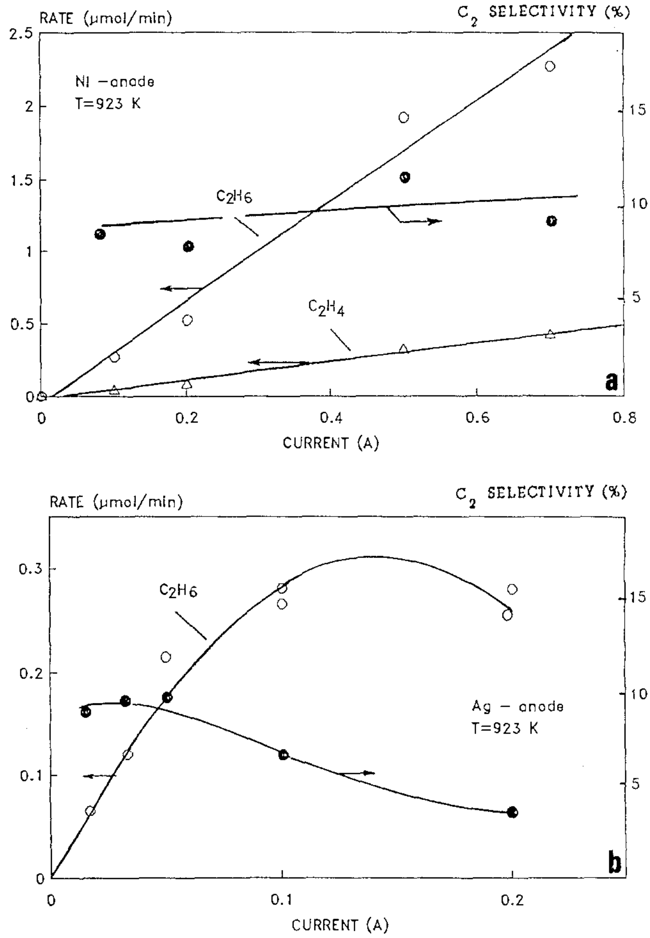

Fig. 4. Effect of current on rate of the formation of C_2-hydrocarbons and selectivity for them over Ni (a) and Ag (b) anodes in the electrocatalytic oxidation of methane.

with the increase of current up to 0.1 A and then reaches a plateau. For this electrode the rate of the formation of C_2H_4 is 20 times lower than that of C_2H_6. This is why figs. 4b and 5 do not demonstrate the rate of the formation of C_2H_4. The selectivity for C_2-hydrocarbons on the Ag electrode decreases from 9 to 3.5% with the increase of current (fig. 4b).

The results presented in figs. 2 and 4, allow the conclusion that C_2-hydrocarbons are formed both under the fuel cell mode of the MCFC operation and under supply of electricity into this systems. However, analysis of the data obtained has shown that the yield of C_2-hydrocarbons with respect to current (current efficiency, CE) appeared to be low values. For the Ni electrode CE is $\approx$ 1.2%. For Ag electrode CE decreases from 1 to 0.4% with the increase of the current.

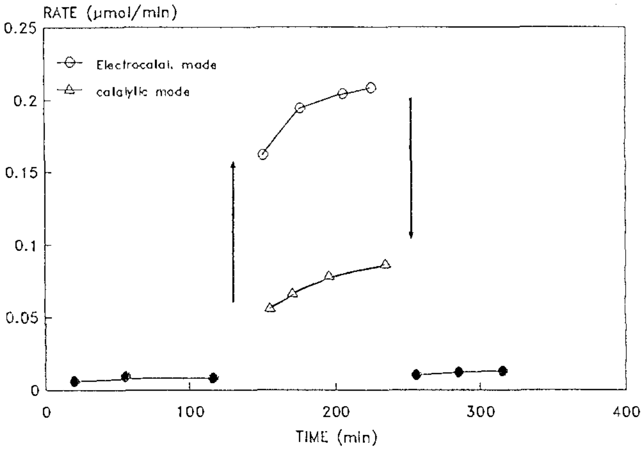

Fig. 5. Rates of the formation of ethane versus time in the electrocatalytic and catalytic modes of the oxidation of methane over Ag electrode at the same oxygen feeding. Arrows indicate the moment of switching on (↑) and off (↓) the oxygen feeding.

We think that the low values of selectivity for C_2-hydrocarbons and of their yield with respect to current upon methane oxidation under the electrocatalytic mode are connected with two points: (i) the compositions of the used electrode-catalysts were far from the optimum; (ii) the operation temperature of the MCFC was lower by ≈ 100 K than the typical temperature of oxidative coupling of methane.

The formation of C_2-hydrocarbons during methane oxidation under the electrocatalytic mode may proceed both with the direct participation of electrochemical steps and without their direct participation. In the latter case, for instance, the carbonate ions can firstly produce oxygen, which is evolved into a gas phase according to reaction 2. Then C_2-hydrocarbons are formed in the same way as under a conventional catalytic mode, when the electric circuit of the cell is opened and oxygen is premixed in the methane flow.

To elucidate if electrochemical steps take part in the formation of C_2-hydrocarbons, we carried out a comparative study of oxidative coupling of methane on Ag electrode in electrocatalytic and conventional catalytic modes.

Fig. 5 shows the rate of the formation of ethane on Ag electrode against time for both modes. Before the moment which is indicated by the arrow turned to the top, the electric circuit of a cell is opened and oxygen-free methane is fed to the anode compartment of the MCFC. Here the rate of ethane formation is seen to have a negligible value of not above 10^{-2} μmol/min. At the arrowed moment oxygen began to be fed into the reaction zone. Under the electrocatalytic mode (fig. 5, open circles) the circuit of a cell was closed and the current of 0.05 A, that corresponds to an oxygen flow of ≈ 7.8 μmol/min into the reaction zone, passes through it. Under the conventional catalytic mode (fig. 5, triangles) the circuit of a cell remained opened and oxygen (7.7 μmol/min too) was premixed to a methane flow before it was fed into the anode compartment. In both of the modes, supplying oxygen in the reaction zone is seen to lead to an increase in the rate of C_2-hydrocarbons formation.

Rates of the formation of ethane were observed as 0.22 μmol/min for the former mode and 0.07 μmol/min (that is a lower value) for the latter, oxygen conversions being about 100% in both cases. Selectivities for ethane were ≈ 10% for the former and ≈ 3% for the latter.

After the supply of oxygen was stopped (the moment is indicated by the arrow turned to the bottom in fig. 5), the rate of the formation of ethane returns to its initial value.

Data in fig. 5 argue in favor of electrocatalytic mode of oxidative coupling of methane being more appropriate than the catalytic one. That can be accounted for by the contribution, unlike in the catalytic mode, of electrochemical steps in the reaction.

At present, however, it is difficult to identify these steps. One can assume that a species of oxygen such as O^- appears on the surface of an electrode, while CO_3^{2-} ions discharged (electrocatalytic mode). This can occur, e.g., as follows:

$$CO_3^{2-} \rightarrow O^- + CO_2 + e^- . \tag{5}$$

These oxygen species are, following from the works done in the field of heterogeneous catalysis [2,3], considered to be responsible for the reaction of oxidative coupling of methane. In particular, this is the interaction between CH_4 and the O^- which is considered to produce $CH_3^{\cdot}$ radicals whose further recombination results in the formation of ethane.

Electrochemical step 5 seems to cause a higher concentration of O^- species on the surface of an electrode if compared to that upon the adsorption of oxygen from a gas phase (conventional catalytic mode). We consider this as a possible explanation for the values of the selectivity for ethane and the rate of its formation in the reaction of CH_4 oxidation under electrocatalytic mode being higher than those under conventional catalytic mode.

Further studies are needed to improve the MCFC anode performance and to elucidate the mechanism of oxidation of methane to C_2-hydrocarbons by CO_3^{2-} ions (oxygen) transported electrochemically through the molten carbonate electrolyte.

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