Catalysis Letters 8 (1991) 61–66

ELECTROCATALYTIC METHANE COUPLING IN THE ABSENCE OF OXYGEN ON A HIGH-TEMPERATURE PROTON-CONDUCTING ELECTROLYTE

L.S. WOLDMAN and V.D. SOKOLOVSKII

Institute of Catalysis, Siberian Branch of the USSR Academy of Science, Novosibirsk 630090, USSR

Received 4 October 1990; accepted 7 November 1990

Methane coupling, electrocatalysis, proton conductive solid electrolyte oxide electrode, C_2-hydrocarbons

Electrocatalytic reaction of methane on the $La_{0.6}Sr_{0.4}MnO_3$ (LSM) anode of electrochemical cells based on $SrO(CeO_2)_{0.95}(YbO_{1.5})_{0.05}$ (SCY) as a high-temperature, proton-conducting solid-electrolyte yields ethane and ethylene. Electric current is generated at zero voltage when methane is present in the anode compartment.

1. Introduction

Recently methane coupling has attracted considerable attention – [1–4]. Usually this reaction is carried out on oxide catalysts, typical examples being alkali earth (often doped by alkali metals) [5], some rare earth oxides [6] or mixed oxides, silicates [7] and other systems [8,9] in the presence of oxygen or other oxidants [1–4]. This reaction also yields CO and CO_2 as by-products, which appear mainly because of the presence of oxygen in the reaction mixture. CH_3 radicals generated in the primary reaction [10,11] interact with the oxygen and yield peroxoradicals which are implicated in the production of the CO and CO_2.

Methane oxidative coupling can also be carried out in electrochemical cells based on O^{2-} conductive solid electrolytes [12–14]. In such cells oxygen is supplied to the reaction mixture through the electrolyte and reacts mainly as adsorbed species. Decreased concentration of gas-phase oxygen leads to increased C_2 selectivity as compared with the ordinary, catalytic reaction. Even so CO and CO_2 still appear as by-products.

In the present study we attempted to carry out methane coupling without any chemical oxidant on the anode of electrochemical cells. We used proton-conductive solid electrolytes to remove hydrogen from the reaction mixture. Thus C_2-hydrocarbons and hydrogen can be obtained separately in the anode and cathode compartment respectively. Earlier ([15]), a high-temperature proton-conductive solid electrolyte was reported to be used for the ethane dehydrogenation in the presence of H_2O vapor. The corresponding setup has not yet been used for methane coupling. But in the course of performing our investigations we learned of a relevant Japanese patent [16], which describes the production of ethylene from the methane used in an electrochemical reactor based on solid, proton-conductive electrolytes. Our work is quite independent, and the experimental details and the direction of our investigations differ from those of the Japanese patent.

2. Experimental

Methane coupling was carried out in an electrochemical cell based on SCY high temperature proton conductive solid electrolyte [17]. The electrolyte material was produced by co-precipitation of cerium and strontium cations by ammonium carbonate from the nitrate solution; Yb was added as Yb_2O_3. The precipitant mixed with Yb_2O_3 was dried at 180 ° C, ground into powder and pre-heated at 1100 ° C for an hour before grinding for a second time. It was then pressed under a pressure of 5 kbar to form a pellet and heated at 1600 ° C for 2 hours. The diameter of the pellet was 22 mm and it was 0.5 mm thick. Each face of the pellet was covered by porous electrodes. The electrode materials used were platinum for the cathode and $La_{0.6}Sr_{0.4}MnO_3$ as anode. Platinum black and anode material were prepared as in [18] and [19] respectively. The electrode material paste with the ethanol solution of rosin was baked to the pellet surface at 1250 ° C for the anode and at 900 ° C for the cathode; the electrode area was 2 cm^2.

The scheme of the electrolyzer is illustrated in fig. 1. One end of the ceramic tube (1), with the electrolyte disk (2) attached, is placed into the heater (3). The anode faces the ceramic tube whereas the cathode is outside. Platinum wire 0.5 mm (4) was attached mechanically to the surface of each electrode. The working gas was supplied to the anode compartment and the flow rate was 4 to 16 ml/min. In different experiments we used CH_4; $CH_4 + H_2O$; $CH_4 + N_2$ or N_2 as

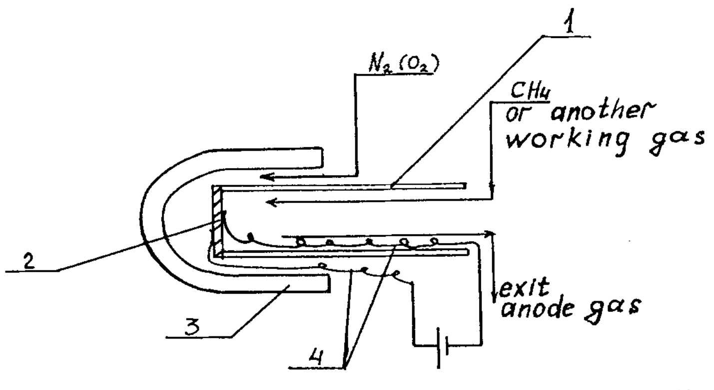

Fig. 1. Scheme of electrolyzer: (1) ceramic tube, (2) electrolyte disk, (3) furnace, (4) platinum wire.

working gases. Exit anode gas was analyzed by GLC. The cathode was exposed to nitrogen and the flow rate was 20 to 30 ml/min. When the cathode was not exposed to N_2 during electrolysis the electrolyte disk lost its conductivity soon after and became brittle. It seems to be due to reduction of Ce^{4+} to Ce^{3+} by the hydrogen generated at the cathode surface. It should be emphasized that the Pt cathode was used also as the reference electrode. The products were analysed chromatographically.

2.1. ELECTROCATALYTIC COUPLING OF METHANE

At temperature about 800 °C methane cracking takes place and ethane and ethylene are obtained as the primary products [20–21]. Consistent with the latter we obtained ethane and ethylene in the exit anode gas at zero applied voltage. When the CH_4 flow rate was 4–16 ml/min there were no other products and no electrode carbonization. (The cathode was exposed to N_2.) The ratio of ethylene to ethane decreased with the increase of the methane stream, in accordance with the consequent conversion CH_4 to C_2H_6 and then to C_2H_4.

When we applied 9 V to the electrodes, the C_2-hydrocarbon concentration in the exit anode gas became 2.5 times as high as at zero voltage. This fact confirms the electrocatalytic methane coupling:

anode $CH_4 - e^- \rightarrow CH_3 + H^+$

cathode $H^+ + e^- \rightarrow \frac{1}{2}H_2$

$$2\,CH_3 \rightarrow C_2H_6$$

anode $C_2H_6 - 2e^- \rightarrow C_2H_4 + 2\,H^+$.

The quantitative results are presented in table 1.

In order to define the current intensity owing to the methane conversion, measurement of current–voltage were taken in two different experiments illustrated in fig. 2. In the first , methane was supplied to the anode compartment (curve a), and in the second experiment N_2 was supplied (curve b). Curve b reflects the electron (not ion) current appearing in the absence of proton sources. Fig. 2 shows that the current corresponding to the methane conversion at 9 V (I_{CH_4}) (difference between curves (a) and (b) at 9 V) is 4.55 mA. We should

Table 1
C_2-production in the electrocatalytic methane coupling

I_{CH_4} (mA)	U (V)	$[C_2H_6]$ (%)	$[C_2H_6]$ (%)	$[C_2]$ (%)
0.65	0	$2.3\cdot10^{-2}$	$6\cdot10^{-3}$	$2.9\cdot10^{-2}$
4.55	9	$5.7\cdot10^{-2}$	$1.7\cdot10^{-2}$	$7.4\cdot10^{-2}$

$v_{CH_4} = 4$ ml/min, $T = 815\,°C$.

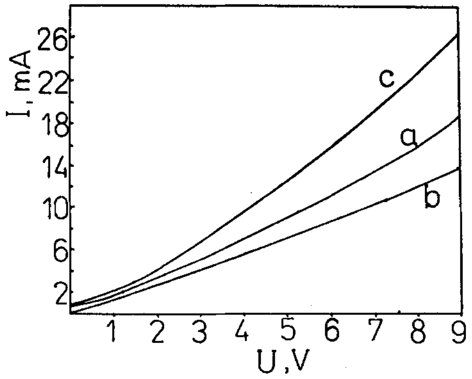

Fig. 2. Current-voltage dependence. (a) working gas CH_4 (N_2 cathode gas); (b) working gas N_2 (N_2 cathode gas); (c) working gas CH_4 (O_2 cathode gas).

emphasize that, at zero voltage, $I_{CH_4} \neq 0$ and equals 0.65 mA. This fact will be discussed later.

From the analysis of table 1 and fig. 2 we calculated that at the applied voltage 9 V Δ $[C_2] = 4.5 \cdot 10^{-2}$ % in the exit gas is connected with the $I_{CH_4} = 4.55–0.655 = 3.9$ (mA). Keeping in mind that 3 electrons are required for one molecule of the C_2 product, the current-efficiency of the methane reaction was calculated to be approximately 12%.

2.2. ELECTROCATALYTIC METHANE COUPLING IN THE PRESENCE OF WATER VAPOR

Often the SCY electrolyte is used for electrolysis in the presence of water vapour [15,22,23] as a source of protons. So we carried out electrocatalytic and ordinary catalytic experiments using 93.5% CH_4 + 6.5% H_2O mixture as a working gas. Comparing the products with those obtained earlier shows that in this system C_2-hydrocarbons can also be obtained in the electrocatalytic reaction. However their concentration is lower by a factor of 2 to 3 than for dry CH_4 working gas (see table 2). This indicates the methane–water competition in the oxidation on the LSM anode. The current efficiency (η) for humid methane was 6.5%. The decrease of the η value in comparison with the dry methane experiments may be attributed to CO and CO_2 by-products.

Table 2
C_2-production in electrocatalytic methane coupling in $CH_4 + H_2O$ mixture

Δ $[C_2H_6]$ (%)	$1.1 \cdot 10^{-2}$
Δ $[C_2H_4]$ (%)	$1.0 \cdot 10^{-2}$
Δ $[C_2]$ (%)	$2.1 \cdot 10^{-2}$

$v = 4.6$ ml/min; $T = 820\,°C$; Δ-denotes the difference in electrocatalytic and ordinary thermal reaction.

Table 3
Currents in SCY cell at zero voltage (different CH_4 concentrations)

CH_4 (%)	another gas (%)	I (mA)	cathode gas (%)
100	–	0.65	N_2
50	50(N_2)	0.35	N_2
93.5	6.5(H_2O)	0.2	N_2

$T = 815$ ° C.

3. Appendix

We have emphasized above the non-zero I_{CH_4} at zero voltage applied when methane was in the anode compartment. It seems to be of particular interest that the I_{CH_4} value depends on methane concentration and can be used for its measurement (see table 3). We draw attention to the essential current changing when methane is humid (table 3). Therefore it is better to use dry methane.

4. Conclusions

We have detected the electrocatalytic reaction of methane coupling without any chemical oxidant on the LSM anode of the electrochemical cell consisting of SCY solid, proton-conductive electrolyte. We obtained very low methane conversion but it can be increased significantly by increase of electrodes area or decrease of the methane flow rate or dilution by inert gas. We can decrease the expenditure of electrical energy using cathode-blowing by O_2 (see fig. 2c). In this case, at the same voltage as for the N_2-blowing situation, we can obtain higher current and higher methane conversion. But, more important, is to increase current, efficiency and here the anode material plays the main role. The testing of other oxide materials is under investigation.

We have found that this work could lead to a new kind of methane sensor.

Acknowledgment

The authors thank V.P. Gorelov who advised us on the electrolyte preparation and S.S. Shepelev for the help in analysis.

References

[1] J.R. Anderson, Appl. Catal. 47 (1989) 177.
[2] H.M. Minachov, N. Ya. Usachov et al., Uspekchi Kchimii 57 (1988) 385.
[3] S. Lee and S.T. Oyama, Catal. Rev. 30 (1988) 249.

[4] G.J. Hutching, M.S. Scurrel and J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.
[5] Ken-ichi Aika and J. Nishiyama, Catal. Today 4 (1989) 271.
[6] S.J. Korf, J.A. Roos, J.M. Diphoorn et al., Catal. Today 4 (1989) 279.
[7] J.M. Thomas, X. Kuan and J. Stachurski, J. Chem. Soc. Chem. Comm. (1988) 162.
[8] H. Nagamato, K. Amanumma and H. Nobutomo, Chem. Lett. (1988) 237.
[9] I. Lee and K.Y.S. Ng, Catal. Lett. 2 (1989) 403.
[10] D.E. Driscoll, W. Martir, J-H. Wang and J.H. Lansford, J. Amer. Chem. Soc. 107 (1985) 58.
[11] D.E. Driscoll and J.H. Lansford, J. Phys. Chem. 89 (1985) 4415.
[12] K. Otsuka, K. Suga and Y. Ichiro, Chem. Lett. (1988) 317.
[13] N.U. Pujare and A.F. Sammells, J. Electrochem. Soc. 135 (1988) 2444.
[14] V.D. Belyaev, V.A. Sobyanin, V.A. Argannikov and A.D. Neuymin, Doklady AN of the USSR 305 1389.
[15] H. Iwahara, H. Uchida and S. Tanaka, J. Appl. Electrochem. 16 (1986) 663.
[16] Imai Techuja and Ishida Kedzo, patent 62-240777, Japan.
[17] H. Iwahara, T. Esaka, H. Uchida and N. Maeda, Solid State Ionics 3/4 (1981) 359.
[18] Yu.V. Karyakin and I.I. Angelov, Clean chemical substances (M. Khimiya, 1974) 407.
[19] D.W. Jahnson, K. Patrick, K. Gallagher et al., Amer. Ceramic. Soc. Bull. 55 (1976) 520.
[20] A.M. Gaffney, USA patent N 4499324.
[21] F. Troliant and Y. Chuin Tin, J. Chin. Chem. Soc. 29 (1982) 265.
[22] H. Iwahara, H. Uchida and I. Ymasaki, Int. J. Hydrogen Energy 12 (1987) 73.
[23] H. Iwahara, H. Ushida and J. Kondo, J. Appl. Elektrochem. 13 (1983) 365.