ELSEVIER

Chemical Engineering Journal 131 (2007) 15–22

Chemical Engineering Journal

www.elsevier.com/locate/cej

Reaction induced current generation by butane oxidation in high temperature electrochemical membrane reactor

L. Chalakov [a], L.K. Rihko-Struckmann [b,*], B. Munder [b], H. Rau [a], K. Sundmacher [a,b]

[a] *Otto-von-Guericke University Magdeburg, Chair for Process Systems Engineering, Universitätsplatz 2, D-39106 Magdeburg, Germany*
[b] *Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, D-39106 Magdeburg, Germany*

Received 24 April 2006; received in revised form 23 November 2006; accepted 27 November 2006

Abstract

The electrocatalytic *n*-butane oxidation has been investigated in an electrochemical membrane reactor with yttria-stabilized zirconia as a solid electrolyte and Pt as cathodic and Au as anodic electrode material, respectively. Vanadyl pyrophosphate (VPO) catalyst layer was deposited on the anode. The investigations of butane partial oxidation were carried out at temperatures between 823 and 873 K in semi-batch and continuous operating mode. The desired product maleic anhydride was detected in the product stream simultaneously as electrical current was generated in the system. The catalyst performance and the induced current level were stable over some hours of operation, after which the catalyst activity gradually reduced due to the insufficient oxygen supply. The reduced catalyst was rejuvenated easily by re-oxidation. In the semi-batch operation mode, pulses of the induced current were observed depending on the hydrocarbon concentration and the oxidation reactions, which were occurring in the anodic compartment.

Keywords: Electrochemical membrane reactor; Butane oxidation

1. Introduction

The low alkanes, propane and butane, can be easily obtained from liquefied petroleum gas (LPG). Butane is used mostly as a clean fuel for domestic purposes or in gasoline to increase its volatility. However, butane and propane can also be used as feedstock in the production of chemical intermediates. Valuable oxygenated compounds and alkenes are produced in the partial oxidation or dehydrogenation processes of low alkanes. Partial oxidation reaction is challenging to implement industrially, because the oxygenated intermediates possesses higher reactivity with oxygen as the primary hydrocarbons. Therefore, the only industrially applied direct partial oxidation process of an alkane, is the oxidation of *n*-butane to maleic anhydride (MA) using vanadyl pyrophosphate (VPO) as catalyst. The MA production is carried out either in packed, fluidized, or transport-bed reactors (riser regenerator). At the process temperature 673 K, the *n*-butane concentration might not exceed 1.2% in packed bed reactors, 4% in fluidized bed reactors and transport-bed reactor, because of the flammability limit of *n*-butane in air [1]. A butane conversion of 80% and selectivity of 70% are typical under these conditions. With optimized oxygen distribution over the reaction zone one might be able to increase the yield of the process further.

The application of membrane reactors for controlled addition of oxygen in the partial oxidation processes has obtained considerable attention during the recent years. Laboratory scale investigations with packed bed VPO catalyst in membrane reactors for *n*-butane oxidation to MA have been carried out by Mallada et al. [2] (PBMR, porous membrane reactor), Mota et al. [3] (MFI zeolite membrane reactor), and Xue and Ross [4] (tubular reactor with α-Al_2O_3 porous membrane). Alonso et al. [5], in turn, applied external fluidized bed for better O_2 distribution along the porous membrane in order to avoid hot spots inside the VPO catalyst layer. Electrochemical membrane reactors with solid oxide membranes for *n*-butane oxidation have been investigated as well [6]. Suitable oxygen ion-conductive membrane materials are e.g. Ca, Mg, Sc, Ti and Y stabilized zirconias (CSZ, MSZ, ScSZ, TiSZ and YSZ) [7–9], Sm doped Ce (SDC) [10] and perovskitic materials like lanthanum gallate (LSGM) [11]. The most frequently used electrolyte in electrochemical membrane reactors material is YSZ, due to its moderate cost, high

---

[*] Corresponding author. Tel.: +49 391 6110318; fax: +49 391 6110566.
E-mail address: rihko@mpi-magdeburg.mpg.de (L.K. Rihko-Struckmann).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.11.018

ionic conductivity and high chemical and mechanical stability. ZrO_2 is a fluorite-type dioxide, where the metal ion (Zr^{4+}) is located in the center of a cube formed by eight oxygen ions. As a charge compensation, the substitution of Zr^{4+} by a trivalent ion (e.g., Y^{3+}) creates oxygen vacancies, which are responsible for the ionic conductivity. The mobility of the oxygen ions depends prevailing on the activation energy, which is required for the position exchange.

The total oxidation of *n*-butane for electrical energy production with solid oxide fuel cells (SOFC) applying YSZ-membranes was examined among others by Sammes et al. [12], Hayashi et al. [13] and He et al. [14]. The observed rapid carbon deposition was due to the oxygen deficit on the anode. Sammes et al. [12] and He et al. [14] attempted to counteract the formation of carbonaceous deposits by increasing the oxygen-to-butane ratios. The partial butane oxidation to MA with an electrochemical membrane reactor (EMR) was demonstrated by Ye et al. [15]. To enhance the oxygen flux through the solid electrolyte membrane by temperatures about 753 K, the electrical current between the two electrodes was supported by external power source in the electrochemical oxygen pumping mode (EOP) [15,16]. However, more challenging is the utilization of the Gibbs free energy change of the oxidation reaction for electrical current generation without external power source as used in fuel cells [17]. In an optimal case, the co-generation mode enables the simultaneous production of chemicals and the direct conversion of the chemical energy to the electrical one. To our knowledge, methane is so far the only alkane investigated in detail in co-generation mode with oxygen ion-conducting SE-membrane. Hibino et al. [18] and Ishihara et al. [11] demonstrated methane oxidation to synthesis gas, and Tagawa et al. [19] to ethane, ethene and carbon monoxide. Iwahara et al. [20] carried out the oxidative dehydrogenation of ethane in the fuel cell operation mode applying H^+ solid-state electrolyte as membrane. All the cited contributions applied either planar or tubular geometry of the ceramic membrane. All these configurations separate completely the educts and overcome therefore the problem of the low flammability limit of hydrocarbons in air. The tubular geometry provides additionally a sealing-free construction in the heated zone of the reactor.

In this contribution we present a detailed study of current generation by butane oxidation in a tubular electrochemical membrane reactor working without external power source. Furthermore, the functionality and the limitations of this reactor concept is evaluated and analyzed.

2. Experimental

2.1. EMR preparation

A schematic illustration of the EMR used in the experimental investigations is shown in Fig. 1. The solid electrolyte membrane applied in the reactor was an one-end closed Y_2O_3-stabilized (8 mol%) ZrO_2 (YSZ) ceramic tube (Viking Chemicals, Denmark). The electrical conductivity of the YSZ solid electrolyte was 3.7×10^{-2} S/cm at 1073 K (specification data from Viking Chemicals). The length of the reactor was 200 mm; inner and outer diameters being 6 and 8 mm, respectively. Initially, the reactor was thermally treated under air at 1173 K for 4 h. The cathode was prepared to the inner surface on the tube by pasting a platinum layer (Chempur No. 900487, Germany). After drying at 373 K for 6 h, the prepared platinum electrode was calcined at 1123 K for 2 h. A platinum wire of 0.125 mm diameter (Chempur No. 009342) was fixed to a 10 cm × 10 cm Pt-gauze (Chempur No. 900338), which was rolled over a 4-bore Al_2O_3-tube with outer diameter of 4 mm. The alumina tube was inserted into the YSZ-tube as an insulator for protecting the three wires (a current carrier Pt as well as Pt and Pt10%Rh wires forming a thermocouple type S) and providing one bore for cathodic air supply. The Pt-gauze guaranteed an undisturbed electric contact between the Pt wire and the cathodic Pt-electrode. Gold (Chempur No. 902904), which was pasted on the outer surface of the solid electrolyte, acted as a current collector at the anode. The electrode area was 26.1 cm^2. A gold wire of 0.25 mm diameter (Chempur No. 009163) was affixed to the porous gold layer. After drying at 373 K for 6 h, the gold electrode was calcined at 1073 K for 2 h.

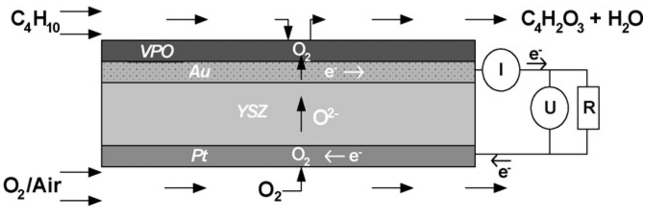

Fig. 1. Working principle of the electrochemical membrane reactor for partial *n*-butane oxidation.

2.2. Catalyst preparation and characterization

The VPO catalyst precursor was prepared by adding 57.0 g of 85% phosphoric acid and 43.3 g of 97.6% phosphorus acid to a mixture of 85.0 g of V_2O_5 and 290 ml of water according to a US patent by Mount et al. [21]. The mixture was refluxed for 12 h. After that, most of the water was evaporated, and the outer surface of the solid electrolyte membrane was coated with the obtained light blue viscous suspension by dipping the reactor several times to the precursor suspension. The reactor with the prepared precursor was dried in a tubular oven at 353–373 K by continually turning it. As a final preparation step, the reactor was calcined in N_2 flow for about 6 h at 823 K, and the catalyst was activated with 1.5 mol% butane in air for 6 h at 823 K.

The specific surface area of the precursor and the activated fresh catalyst was measured by the BET method with N_2 adsorption at 77 K with Micromeritcs ASAP 2010 instrument. The precursor and the fresh catalyst had the BET surface areas of 2 and 5 m^2/g, respectively. X-ray diffraction analyse (XRD) of the fresh catalyst with X-ray diffractometer D500 Bruker/AXS with Cu Kα radiation at ambient temperature revealed a co-existence of $(VO)_2P_2O_7$ and $VOPO_4$ phases; whereas the clear majority was the $(VO)_2P_2O_7$-phase.

2.3. Experimental setup

The membrane reactor was fixed inside a quartz glass tube (Fig. 2a), which was located in a tubular oven (LMK 1200-40-300 HTM Reetz, Germany). The experiments were carried out either in a semi-batch or continuous mode in relation to the anodic gas recycle. In a semi-batch mode the reactor was operated by injecting 0.6 or 1.2 ml butane to the anodic gas cycle (approximately 300 cm^3) corresponding to an calculated averaged butane concentration of 0.2 and 0.4 vol.%. Some investigations were carried out in a continuous, once-through mode with constant butane concentration at the anodic side under ambient pressure (see Fig. 2b). An atmospheric oxygen partial pressure was applied at the cathodic side. The anodic recycle gas flow rate was between 50 and 200 cm^3/min in the semi-batch mode, and the reactor was operated at temperatures between 823 and 873 K. The external electrical current between the electrodes applying a low-resistance amperometer was recorded during the experiments. The anodic gas was circulated through an ice trap (273 K) at the reactor exit in order to collect the produced MA into the water in the trap. A qualitative indication of the maleic anhydride formation was obtained by following the conductivity change of the water in the trap during the experiments. The existence of MA in the trap water was confirmed by a subsequent ion chromatographic analysis (Dionex, USA). The concentration of the butane in the anodic recycle gas was analyzed with a gas chromatograph (8340 FISONS Instruments), equipped with a flame ionization detector (FID). Due to the very low concentrations of the products, it was not possible to determinate MA, CO, CO_2 quantitatively with the gas chromatograph. The carbon content in the used and fresh VPO catalyst was determined with a LECO CNHS-932 analyzer.

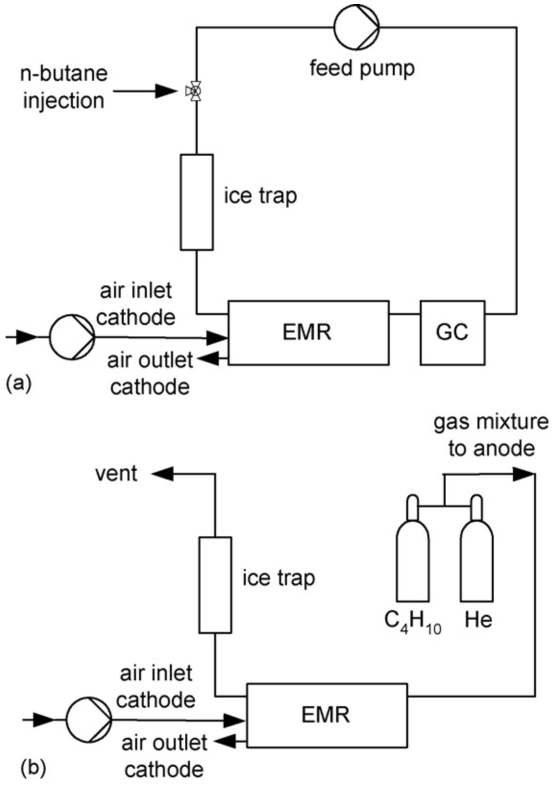

Fig. 2. Schematic illustration of the experimental setup: (a) semi-batch and (b) continuous operating mode.

3. Results and discussion

Prior to the electrochemical experiments, the catalyst activity was tested separately with butane–air mixture (0.2 vol.%) at 673 K. The ion chromatographic analysis of the trap water confirmed the formation of maleic anhydride with the activated VPO catalyst.

3.1. Semi-batch operation of EMR in butane oxidation

The electrochemical oxidation of *n*-butane to MA were carried out initially in the semi-batch modus with a reactor configuration of VPO|Au|YSZ|Pt. To remove possible carbon decompositions from the VPO surface formed in previous experiments, the reactor was flushed for 20 min with air prior to a new experiment. After the air flushing, the reactor was first treated with nitrogen for about 30 min, and subsequently a known volume of *n*-butane was injected into the anodic compartment.

The effect of the residence time on the MA production was investigated by varying the gas recycle rate between 50 and 200 ml/min. The residence time in the recycle modus was defined as follows:

$$\text{residence time (s)} = \frac{\text{reactor volume}}{\text{gas recycle rate}},$$

where the reactor volume is the volume of the anodic compartment. Assuming here that the conductivity in the trap water correlates directly with the concentration of MA, the result was unequivocal—a shorter residence time preferred the MA production as seen in Fig. 3. The desired product is an unstable intermediate, which is easily over-oxidized to carbon oxides to higher extent at longer residence time. Based on the obtained

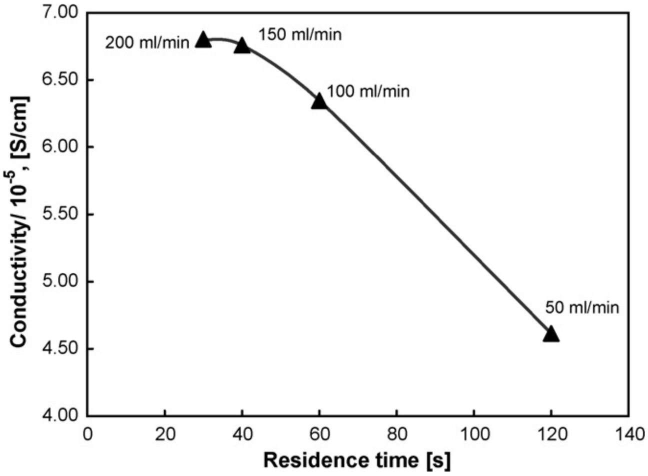

Fig. 3. The conductivity of the trap water as a function of the residence time. $T = 873$ K; anode: 0.4 vol.% *n*-butane in He, flow rates between 50 and 200 ml/min; cathode: air, flow rate 100 ml/min.

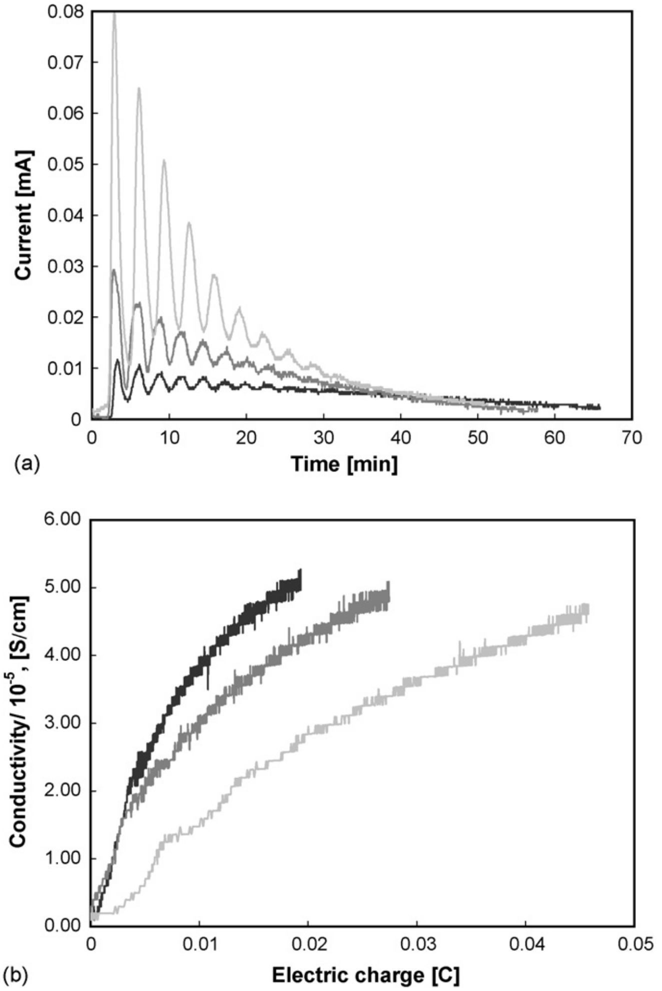

Fig. 4. (a) The current generation as a function of time and (b) the conductivity of the trap water as a function of the transferred electric charge at temperatures 823 K (—), 848 K (▬), and 873 K (▬). Anode: 0.2 vol.% *n*-butane in He, flow rate 150 ml/min; cathode: air, flow rate 100 ml/min.

results, in the following experiments mostly a gas flow rate of 150 ml/min was applied.

The semi-batch experiments were carried out at temperatures 823, 848 and 873 K. The lower limit, 823 K, is approximately 100 K higher than the temperature used in the industrial fixed, fluidized or circulating fluidized bed reactors. The highest applied temperature, 873 K, is about 100 K lower than the temperature usually in SOFCs. The selected temperature range is a compromise, as a high operating temperature is desired in the EMR in order to obtain high oxygen flux through the electrolyte membrane, but on the other hand, a low operating temperature (below 673 K) is favorable for the catalyst selectivity.

The reaction induced current in the semi-batch experiments was found to change periodically over the reaction time as illustrated in Fig. 4a. The injected butane reached the anodic compartment of the membrane reactor in about 1.5 min after the injection. The reaction induced current increased sharply and it achieved its maximum after approximately 3 min. The maximum current of 0.15 mA obtained at 873 K during the first pulse corresponds to oxygen transfer rate of 3.89×10^{-10} mol/s (1.49×10^{-11} mol/(s cm^2)). Oscillation of current was observed as the injected butane in the recycle gas reached repeatedly the reactor. The subsequent current pulse was always smaller than the previous one, because the butane was likely consumed by the oxidation reactions. The peaks did not broaden considerably during one experiment indicating a minor back-mixing effect. After approximately 10 peaks the butane was completely converted and the current signal reached its initial level. Gas chromatographic analysis of the anodic gas mixture confirmed that the butane was totally converted. The highest current peaks (see Fig. 4a) were achieved expectedly at the highest temperature, 873 K, due to the improved permeability of the electrolyte to oxygen ions at higher temperatures.

Fig. 4b illustrates the correlation between the measured conductivity in trap water and the total charge transferred during one experiment. Here, the highest transferred charge (45 mC) at 60 min reaction time was obtained at the highest operating temperature, and the lowest transferred charge (20 mC) at the lowest temperature. However, an inverse correlation was observed in the conductivity of the trap water. As the highest conductivity was measured at the lowest experimental temperature, which suggests that the MA formation was highest at the lowest temperature. Higher temperature in the reactor increased the total transferred charge but lowered the MA selectivity. The increased transferred charge was likely due to the increased formation of the undesired total oxidation products CO and CO_2. Therefore, we got here the clear indication that the selectivity to the total oxidation products became obviously more favorable at increased working temperature.

The effect of butane concentration on the induced current was investigated at temperature 873 K. Fig. 5a and b illustrates the current and the corresponding conductivity of the water in the trap measured on-line as a function of time with butane injections of 1 and 2 ml, respectively. The current increased clearly as the injected butane amount was doubled. The observed current peaks were higher and the total reaction time increased due to the higher driving force of the process. The conductivity of the water in the trap was also found to correlate directly with the butane concentration, the higher conductivity was observed with higher butane concentration. The initially measured open circuit voltage (OCV) for both butane injections were 133 mV, respectively, 164 mV. However, here should be mentioned that obtained OCV values were very sensitive depending on the electrochemical membrane reactor construction and were unique for each cell as observed with measurements with several prepared cells. Moreover, only a small change in the anodic gas composition changed immediately the OCV value. It is well known, that the electrochemical cell reacts instantaneously to oxygen concentration changes, which also enables the use of symmetrical cells like Pt|YSZ|Pt as sensors for fast on-line monitoring of oxygen concentration. Higher hydrocarbon concentrations than were tested as well, and the induced current increased expectedly to some extent, but already at butane averaged concentration of 0.6 vol.% deactivation due to electrode surface coking was observed.

In order to investigate the catalyst and the reactor stability, we carried out one experiment in the semi-batch mode with five successive butane injections at time interval of about 60 min each.

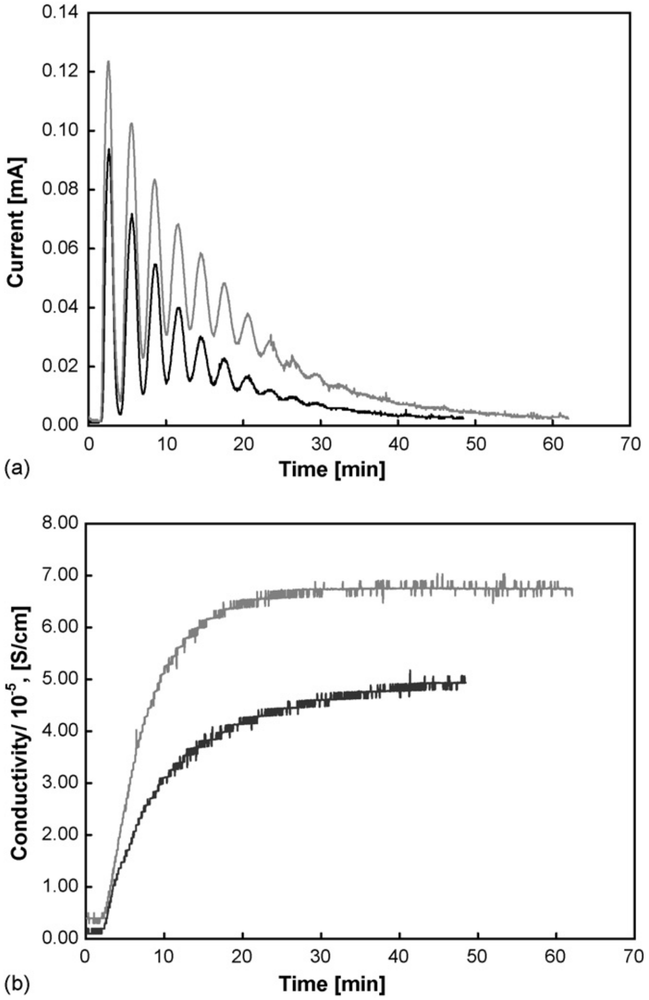

Fig. 5. (a) The current generation and (b) the conductivity of the trap water as a function of time at butane concentrations on the anode 0.2 vol.% (—), respectively 0.4 vol.% (▬); $T = 873$ K; flow rate 150 ml/min; cathode: air, flow rate 100 ml/min.

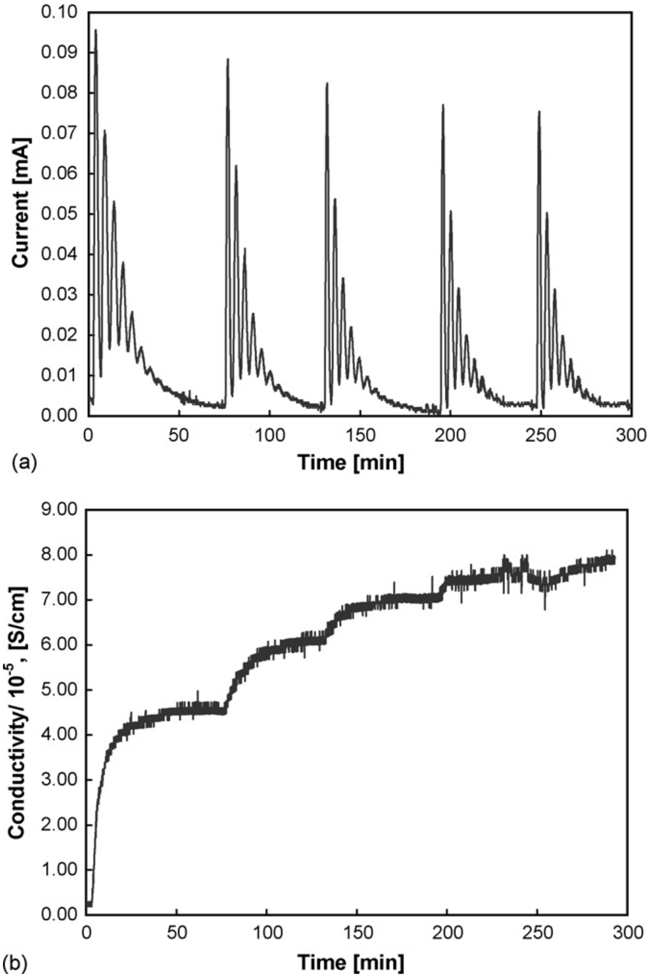

Fig. 6. (a) The current generation and (b) the conductivity of the trap water as a function of time during a long-term experiment. $T = 873$ K; anode: 5×0.6 ml (0.2 vol.%) *n*-butane in He, flow rate 100 ml/min; cathode: air, flow rate 100 ml/min.

The induced current peaks and the transferred electric charge at each injection are illustrated in Fig. 6a. Initially, during the peaks followed the first injection, the transferred electric charge was 0.07 C and the maximal current 0.096 mA, whereas after the subsequential injections both the electric charge as the obtained maximal current decreased as seen in Fig. 6a and in Table 1. Fig. 6b illustrates the changes of the conductivity in the trap water (MA production) during the experiment. The reactor was working stable for 300 min, showing an excellent correlation between the current and MA formation (Fig. 6b). As seen in Fig. 6b, a new incremental step of the water conductivity in the trap correlated to MA formation, was always smaller than the previous one. The decreased selectivity to MA is associated with an increase in CO_x selectivity. The decreasing MA selectivity is probably due to the change in the oxidation state of the catalyst. The highest catalytic activity is observed with the freshly regenerated catalyst at the beginning of the experiment. Due to the reactor performance and the separated reactant supply, the oxygen transport to the VPO layer does not occur fast enough in order to prevent the catalyst reduction, which directly reflects on the achieved results. The oxidation state of the VPO is highly sensitive to the oxygen concentration in the immediate vicinity. We have observed in our earlier studies that the used VPO catalyst applied in EOP investigations showed a remarkable reaction induced difference in the vanadium oxidation state in the radial direction [22]. An increase for the inner catalyst surface (facing the YSZ-membrane) and a remarkable decrease for the outer catalyst surface (facing the butane-rich anodic compartment) were observed with respect of the initial oxidation state of the fresh

Table 1
Current maxima and the electric charge for each butane injection during a long-term experiment

Injection number (–)	First peak time (min)	Current maxima (mA)	Electric charge (C)
1	04.00	0.0957	0.070
2	77.06	0.0884	0.043
3	131.83	0.0825	0.037
4	185.83	0.0771	0.034
5	239.06	0.0755	0.033

$T = 873$ K; anode: 5×0.6 ml (0.2 vol.%) *n*-butane in He, flow rate 100 ml/min; cathode: air, flow rate 100 ml/min.

catalyst. Therefore, the deceasing MA selectivity observed in the present study is most likely explained by the changes of the oxidation state of the VPO catalyst.

3.2. Continuous operation of EMR in butane oxidation

The second set of experiments was carried out in a continuous operation mode (see Fig. 2b). The reactor operation was investigated with butane concentration of 0.2 vol.% in helium at temperature 873 K. As seen in Fig. 7a, considerably higher current values were obtained in the continuous operation compared to those in the semi-batch mode. Initially a maximum current of approximately 0.3 mA corresponding to oxygen transfer of 7.77×10^{-10} mol/s (2.98×10^{-11} mol/(s cm^2)) was achieved. The current decreased slightly over time (see Fig. 7a). The color of the VPO layer changed from yellow-green to gray-black indicating changes in the oxidation state of the catalyst. There are two likely reasons for the color change, either the oxidation of state of the catalyst has been changed or carbonaceous deposits have coved the catalyst surface. According to the investigations of Rodemerck et al. [23] color changes indicate changes in the valence state of vanadium in the VPO catalyst. The catalyst having yellow-green color has high oxidation state. It is well known that lower oxidation states (gray or black color) have a negative influence on the MA selectivity [23]. The formation of carbonaceous deposits was obvious, as the carbon content increased from the initial value of 0.062% (fresh catalyst) to 0.139%.

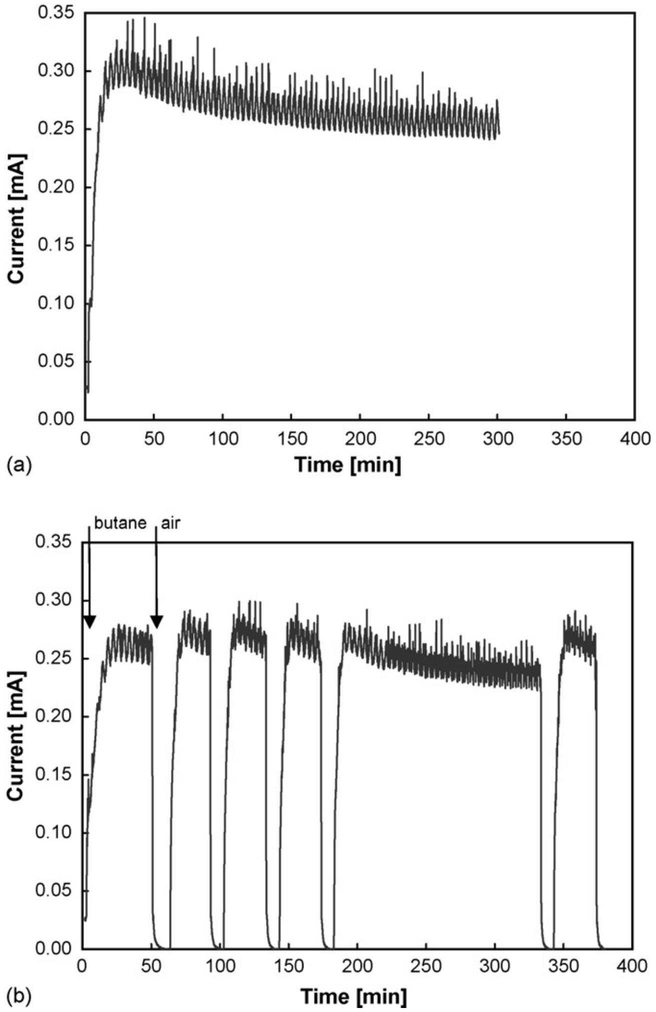

Fig. 7. The current generation as a function of time (a) at continuous operation mode and (b) with periodical catalyst re-oxidation. T = 873 K; anode: 0.2 vol.% *n*-butane in He, flow rate 150 ml/min; cathode: air, flow rate 100 ml/min.

To investigate the long time stability of the system in the continuous operation mode, the catalyst was periodically regenerated switching either butane or air flow to the anodic compartment. As seen in Fig. 7b, the initial activity was reached after each regeneration period, but a relatively fast decrease in the current was observed after the regeneration. During one longer current generation phase of 150 min, the induced current decreased about 15%, but it was easily rejuvenated after the gas phase regeneration.

3.3. The influence of the catalyst to the induced current

In order to bring clearance to the effect of the catalyst VPO to the induced current, we finally carried out measurements with the same Au|YSZ|Pt reactor, but prior to these investigations we removed the catalyst layer from the anode surface. The reactor was tested under identical conditions like the VPO|Au|YSZ|Pt cell (anode: 873 K, 150 ml/min, 0.23 vol.% butane in helium; cathode: 100 ml/min air) in the continuous operating mode. When the external circuit was closed, measurable electrical current was detected also in the absence of VPO catalyst. The initial current level without hydrocarbon in the feed (anode: He; cathode: air) was about 10–15 μA. As the 0.2 vol.% butane was included in the feed, the current increased immediately to a level of about 35–40 μA. We could see here clearly that the current was significantly lower without VPO than in the presence of the catalyst on the anode. The maximal current obtained in the absence of VPO was only about 10–20% of the current observed with a reactor including the VPO layer. The O_2 concentration difference between the cathodic and the anodic atmosphere induced expectedly a small electrical current through the membrane. The observed current increase with butane containing feed gas in the anodic feed could be explained by immediate oxidation reactions on the Au electrode which lowered the oxygen concentration. However, this observation is not in a direct agreement with the observation of Ye et al. where only negligible reactions of butane were observed on the Au anode in the membrane reactor Au|YSZ|Pt–Ag [24]. It should be noticed here that the measurements by Ye et al. were carried out under oxygen pumping mode (EOP), which is not directly comparable with our present study. In addition to this, we might expect here that the changes in the potential difference in the EMR and following current induction is likely more sensitive to the reactor conditions than the gas analyses carried out by Ye et al. Unfortunately, a quantitative analysis of the butane conversion and the selectivities to MA, CO and CO_2 was not possible to obtain in the present investigation, due to the very low concentrations of the products.

As we have seen in the above results, the influence of the catalyst in a reactor VPO|Au|YSZ|Pt is remarkable. In a membrane reactor containing the VPO anodic layer, oxygen reacts to higher extent, increasing the potential difference between the anode and cathode and in such a way the catalyst induces higher current. However, the investigated reactor system was found to be highly sensitive to experimental conditions, and the achieved levels of current undoubtedly depended also on e.g. the cell preparation, membrane and electrode material, amortization of the cell.

All the results presented here were achieved with one reactor. For more than 350 working hours the electrochemical system performed stabile and reproducible results. No membrane embrittlement or other mechanical damages were detected during the reactor operation. Possible damages of the ceramic material are more likely when the membrane reactor is operated in the EOP mode. In the EOP mode the stress for the material is remarkable due to the externally applied potential (thermodynamic decomposition potential of zirconia is 2.5 V at 773 K) between the electrodes. In the present study, the chemical reaction induces considerably lower potential difference between the electrodes, which increases the durability of the membrane reactor.

In an EMR possible oxidation reactions are presented in Fig. 8 and listed in Eqs. (1)–(5) [25]:

$$C_4H_{10} + 3.5O_2 \xrightarrow{r_1} C_4H_2O_3 + 4H_2O, \quad \Delta H_{R,1} = -1239\ \text{kJ/mol} \tag{1}$$

$$C_4H_{10} + 4.5O_2 \xrightarrow{r_2} 4CO + 5H_2O, \quad \Delta H_{R,2} = -1525\ \text{kJ/mol} \tag{2}$$

$$C_4H_{10} + 6.5O_2 \xrightarrow{r_3} 4CO_2 + 5H_2O, \quad \Delta H_{R,3} = -2657\ \text{kJ/mol} \tag{3}$$

$$C_4H_2O_3 + O_2 \xrightarrow{r_4} 4CO + H_2O, \quad \Delta H_{R,4} = -286\ \text{kJ/mol} \tag{4}$$

$$C_4H_2O_3 + 3O_2 \xrightarrow{r_5} 4CO_2 + H_2O, \quad \Delta H_{R,5} = -1418\ \text{kJ/mol} \tag{5}$$

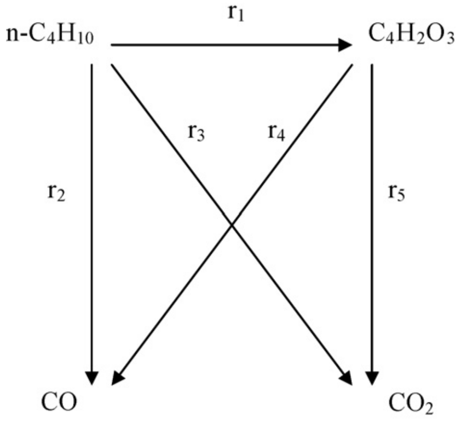

Fig. 8. The reaction network for the *n*-butane oxidation.

As we see all the reactions are highly exothermic including remarkable release of Gibbs free energy, and therefore highly interesting to electrochemical processing. It is to be expected that it is not only the MA formation which induces the detected current in our investigations, but also the total oxidation of butane to CO/CO_2 is highly probable, as observed as competitive reactions to the formation of MA by numerous investigations by Ye et al. under oxygen pumping conditions [15,24,26]. Furthermore, the current might be induced also by the over-oxidation of MA to CO/CO_2 according to reactions (4) and (5) as well. York et al. [6] investigated the electrochemical butane oxidation with an Au|YSZ|Ag cell. At reaction temperature of 723 K and an applied current of 4.5 mA, no MA was detected under electrochemical oxygen pumping conditions, which is in agreement with the observations of Ye et al. [24] with Au|YSZ|Pt–Ag reactor at 753 K. Based on these literature reportings and our own results, we might conclude that the formation of MA is not occurring on the Au electrode surface.

In the presented experimental study only a semi-qualitative analysis of the formed MA was possible due to the very low concentrations of the products. Generally, we might say here that there are many limiting factors in the investigated electrochemical system where the current is induced by the reactions. A high operating temperature would be desired in an EMR in order to obtain high oxygen flux. On the other hand, low operating temperature is favorable for the catalyst selectivity. The electrode preparation process is complicated, and the electrodes are working with high overvoltages. Although the functionality of this reactor concept was proved here, the achieved current levels and the correlating oxygen flux were very low. The maximum reaction induced current in the present investigation, 0.3 mA, corresponds to the oxygen flow of 7.77×10^{-10} mol/s (2.98×10^{-11} mol/(s cm^2)). The operation in EMR with measurable quantitative results is only possible with applied voltage in the EOP modus as reported in [15,24,26]. The applied voltage between the electrodes increased the current more than one order of magnitude (up to 120 mA in the studies of Ye et al.) at the temperatures from 720 to 790 K, where quantitative measurable MA amounts were synthesized.

4. Conclusions

With the electrochemical VPO|Au|YSZ|Pt reactor, used for the process of partial oxidation of *n*-butane in the fuel cell mode, MA was synthesised and simultaneously an induced electrical current was observed. During the butane oxidation, the VPO catalyst deactivated likely due to vanadium oxidation state changes. Furthermore, the formation of carbonaceous deposits on the surface was detected during the experiments which also might influence to the activity, but a regeneration with air rejuvenated the catalyst to the original activity. A detectable electrochemical current was achieved also with an Au|YSZ|Pt reactor without VPO layer as a result of the different oxygen concentration on the anode and the cathode, but the current levels were significantly lower than the ones obtained with the VPO|Au|YSZ|Pt reactor.

Acknowledgements

The financial support by the German Research Foundation (DFG, research unit 447 “Membranunterstützte Reaktionsführung”) is gratefully acknowledged. We also thank Dr. S. Busse (Otto-von-Guericke University Magdeburg, Germany) for the carbon content analysis.

References

[1] G. Centi, F. Cavani, F. Trifido, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/Plenum Publishers, New York, 2001.

[2] R. Mallada, M. Menéndez, J. Santamaria, Use of membrane reactors for the oxidation of butane to maleic anhydride under high butane concentrations, Catal. Today 56 (2000) 191–197.

[3] S. Mota, S. Miachon, J.-C. Volta, J.-A. Dal mon, Membrane reactor for selective oxidation of butane to maleic anhydride, Catal. Today 67 (2001) 169–176.

[4] E. Xue, J. Ross, The use of membrane reactors for catalytic *n*-butane oxidation to maleic anhydride with a butane-rich feed, Catal. Today 61 (2000) 3–8.

[5] M. Alonso, M.J. Lorences, M.P. Pina, G.S. Patience, Butane partial oxidation in an externally fluidized bed-membrane reactor, Catal. Today 67 (2001) 151–157.

[6] A.P.E. York, S. Hamakawa, T. Hayakawa, K. Sato, T. Tsunoda, K. Takehira, Partial oxidation of C2–C4 alkanes into oxygenates using an Au|yttria-stabilized zirconia|Ag electrochemical reaction cell, J. Chem. Soc., Faraday Trans. 92 (19) (1996) 3579–3586.

[7] H.-H. Möbius, H. Witzmann und, G. Pröve, Systematische Leitfähigkeitsmessungen an sauerstoffionenleitenden Festelektrolyten aus Zirkonoxid und Seltenen Erden, Z. Chem. 4 (1964) 81–94.

[8] B.C.H. Steele, Ceramic ion conducting membranes, Curr. Opin. Solid State Mater. Sci. (1992) 684–691.

[9] D. Eng, M. Stoukides, Catalytic and electrocatalytic methane oxidation with solid oxide membranes, Catal. Rev.-Sci. Eng. 33 (3–4) (1991) 375–412.

[10] S. Hamakawa, T. Hayakawa, K. Suzuki, R. Shiozaki, K. Takehira, Electrochemical oxidation of methane to synthesis gas using an oxide ionic conductor, Denki Kagaku 65 (12) (1997) 1049–1056.

[11] T. Ishihara, T. Yamada, T. Akbay, Y. Takita, Partial oxidation of methane over fuel cell type reactor for simultaneous generation of synthesis gas and electric power, Chem. Eng. Sci. 54 (1999) 1535–1540.

[12] N.M. Sammes, R.J. Boersma, G.A. Tompsett, Micro-SOFC system using butane fuel, Solid State Ionics 135 (1–4) (2000) 487–491.

[13] K. Hayashi, O. Yamamoto, H. Minoura, Portable solid oxide fuel cells using butane as fuel, Solid State Ionics 132 (3–4) (2000) 343–345.

[14] H. He, J.M. Vohs, R.J. Gorte, Carbonaceous deposits in direct utilization hydrocarbon SOFC anode, J. Power Sources 144 (2005) 135–140.

[15] Y. Ye, L. Rihko-Struckmann, B. Munder, H. Rau, K. Sundmacher, Feasibility of an electrochemical membrane reactor for the partial oxidation of *n*-butane to maleic anhydride, Ind. Eng. Chem. Res. 43 (2004) 4551–4558.

[16] M. Stoukides, Solid-electrolyte membrane reactors: current experience and future outlook, Catal. Rev.-Sci. Eng. 42 (1 and 2) (2000) 1–70.

[17] K. Sundmacher, L. Rihko-Struckmann, V. Galvita, Solid electrolyte membrane reactors: status and trends, Catal. Today 104 (2005) 185–199.

[18] T. Hibino, K. Ushiki, T. Sato, Y. Kuwahara, A novel cell design for simplifying SOFC system, Solid State Ionics 81 (1995) 1–3.

[19] T. Tagawa, K.K. Moe, M. Ito, S. Goto, Fuel cell type reactor for chemicals-energy co-generation, Chem. Eng. Sci. 54 (1999) 1553–1557.

[20] H. Iwahara, H. Uchida, S. Tanaka, High temperature-type proton conductive solid oxide fuel-cells using various fuels, J. Appl. Electrochem. 16 (1986) 663–668.

[21] R.A. Mount, J.F. Pysz, H. Raffelson, Phosphorus–vanadium–oxygen catalysts having a specific pore volume, US Patent 4,092,269 (1978).

[22] L.K. Rihko-Struckmann, Y. Ye, L. Chalakov, Y. Suchorski, H. Weiss, K. Sundmacher, Bulk and surface properties of a VPO catalyst used in an electrochemical membrane reactor: conductivity-, XRD, TPO- and XPS-study, Catal. Lett. 109 (1–2) (2006) 89–96.

[23] U. Rodemerck, B. Kubias, H.W. Zanthoff, G.U. Wolf, M. Baerns, The reaction mechanism of the selective oxidation of butane on $(VO)_2P_2O_7$ catalysts: the influence of the valence state of vanadium, Appl. Catal. A: Gen. 153 (1997) 217–231.

[24] Y. Ye, L. Rihko-Struckmann, B. Munder, K. Sundmacher, Partial oxidation of *n*-butane in a solid electrolyte membrane reactor influence of electrochemical oxygen pumping, J. Elec. Soc. 153 (2) (2006) D21–D29.

[25] N. Emberger, Zur Reaktionskinetik der Selektivoxidation von n-Butan an einem technischen $(VO)_2P_2O_7$-Katalysator, Ph.D. Thesis, University of Magdeburg, 2005.

[26] Y. Ye, L. Rihko-Struckmann, B. Munder, K. Sundmacher, Partial oxidation of *n*-butane in a solid electrolyte membrane reactor: periodic and steady-state operations, Appl. Catal. A: Gen. 285 (1–2) (2005) 86–95.