Journal of Power Sources 190 (2009) 2–13

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Ethanol electrooxidation on a carbon-supported Pt catalyst at elevated temperature and pressure: A high-temperature/high-pressure DEMS study

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ARTICLE INFO

Article history:
Received 26 January 2009
Accepted 26 January 2009
Available online 6 February 2009

Keywords:
Ethanol oxidation
Elevated temperature
Elevated pressure
DEMS
CO_2 current efficiency
Activation energy

ABSTRACT

The electrooxidation of ethanol on a Pt/Vulcan catalyst was investigated in model studies by on-line differential electrochemical mass spectrometry (DEMS) over a wide range of reaction temperatures (23–100 °C). Potentiodynamic and potentiostatic measurements of the Faradaic current and the CO_2 formation rate, performed at 3 bar overpressure under well-defined transport and diffusion conditions reveal significant effects of temperature, potential and ethanol concentration on the total reaction activity and on the selectivity for the pathway toward complete oxidation to CO_2. The latter pathway increasingly prevails at higher temperature, lower concentration and lower potentials (~90% current efficiency for CO_2 formation at 100 °C, 0.01 M, 0.48 V), while at higher ethanol concentrations (0.1 M), higher potentials or lower temperatures the current efficiency for CO_2 formation drops, reaching values of a few percent at room temperature. These trends result in a significantly higher apparent activation barrier for complete oxidation to CO_2 (68 ± 2 kJ mol^{-1} at 0.48 V, 0.1 M) compared to that of the overall ethanol oxidation reaction determined from the Faradaic current (42 ± 2 kJ mol^{-1} at 0.48 V, 0.1 M). The mechanistic implications of these results and the importance of relevant reaction and mass transport conditions in model studies for reaction predictions in fuel cell applications are discussed.

1. Introduction

Direct ethanol fuel cells (DEFCs) have received growing attention as renewable power sources during recent years [1–8]. The successful introduction of DEFCs is hindered, however, by the slow kinetics of the ethanol electrooxidation reaction and its poor selectivity toward complete oxidation to CO_2 [6,9–16], while much or even most of the ethanol is only partly oxidized to acetaldehyde or acetic acid (see below). The kinetics and mechanism of the ethanol oxidation reaction (EOR) have been investigated extensively in model studies on massive electrodes and supported catalysts electrodes, employing purely electrochemical measurements as well as *in situ* spectroscopic techniques (for a summary see below). Direct transfer of these results to the reaction in a realistic fuel cell, however, is hardly possible because of the very different reaction and mass transport conditions in both cases: While DEFCs are operated at elevated temperatures under enforced electrolyte transport, using high surface area electrodes, model studies are mostly performed at room temperature and in stagnant electrolyte, in the absence of enforced electrolyte transport, and often on massive metal electrodes with low surface area (for reviews see [17,18]). Detailed reaction studies performed using realistic fuel cells, on the other hand, are rare [6,9,14,15,19,20], and the reaction conditions are much less defined than those in model studies and may differ significantly between different studies. For instance, measurements of the CO_2 product yield and CO_2 current efficiency, which were performed in three different studies [6,9,19,20], arrived at widely differing results. Measuring the relative product distribution for ethanol oxidation at the exhaust of a polybenzamidazole (PBI) fuel cell by on-line mass spectrometry (temperature range 150–190 °C), Wang et al. determined acetaldehyde as the main reaction product and CO_2 as a minority product, with the CO_2 content increasing with increasing water-to-ethanol ratio [9]. On the other hand, Aricò et al. reported a high selectivity toward CO_2 formation (95%) for ethanol oxidation in a liquid-feed polymer electrolyte fuel cell with a PtRu/Vulcan anode catalyst (145 °C, 1 M ethanol) [19]. Comparable results were published by Rao et al. for ethanol oxidation over a Pt/C catalyst, who measured the CO_2 concentration at the exhaust of a DEFC by on-line mass spectrometry in the temperature range between 30 and 90 °C and obtained a current efficiency for CO_2 formation of more than 75% at 90 °C (0.1 M ethanol, 5 mg cm^{-2} Pt catalyst loading), whereas for 1 M ethanol oxidation on a PtRu/C catalyst MEA the current efficiency for CO_2 formation was significantly lower [20].

Comparable model studies, which were performed at room temperature in stagnant electrolyte, also led to diverging results on the product distribution [11,12,21,22]. Hitmi et al. determined acetic acid as main product for ethanol oxidation on polycrystalline Pt at

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doi:10.1016/j.jpowsour.2009.01.073

10 °C/0.8 V at low concentrations (<0.01 M), whereas acetaldehyde prevailed at high concentration (>0.1 M) [21]. In contrast, much higher relative yields of CO_2, reaching even 100%, were determined by on-line differential electrochemical mass spectrometry (DEMS) for ethanol oxidation on PtRu electrodes at low temperatures (5 and 25 °C) [22]. On the other hand, rather low current efficiencies for CO_2 formation were obtained in model studies over PtRu and PtRu/C catalysts [23–26]. Without commenting on the very different results of these model studies, it is clear that the reaction conditions are incommensurable with those in fuel cell measurements. Recently, Wang et al. systematically investigated the product distribution of ethanol oxidation over a Pt/Vulcan catalyst as a function of temperature (23–60 °C), ethanol concentration and catalyst loading in a model study by DEMS, using a thin-film supported catalyst (Pt/Vulcan) electrode with negligible diffusion resistance and well defined enforced electrolyte mass transport [10]. Incomplete ethanol oxidation to acetaldehyde and acetic acid was found to prevail over complete oxidation to CO_2 under these experimental conditions, with CO_2 current efficiencies in the range of a few percent at most.

To further approach the situation in a realistic fuel cell, while maintaining the well defined reaction and transport conditions in model studies, it is particularly important to raise the reaction temperature to at least 100 °C, possibly even higher, which also requires pressurizing the reaction cell and the electrolyte to prevent evaporation of electrolyte and reactants. A number of groups reported the build-up of pressurized high-temperature cells [27–37]. These cells allow operation at relevant temperatures, mostly also under controlled and enforced electrolyte transport, but are limited to purely electrochemical measurements.

Recently, we developed a high-temperature/high-pressure DEMS set-up which allows electrocatalytic measurements on supported catalyst thin-film electrodes (ca. 100% catalyst utilization, negligible diffusion limitations) at elevated temperatures (up to 100 °C) and pressure (3 bar overpressure) under continuous reaction and well defined, enforced mass transport conditions [38]. This set-up was employed to investigate the electrooxidation of ethanol on carbon supported Pt/Vulcan catalysts at temperatures up to 100 °C under well defined and fuel cell relevant reaction and transport conditions. Although from experimental reasons we can not discriminate between acetaldehyde and acetic acid product formation at present (see Section 2), this allows us to discriminate between partial oxidation (acetaldehyde, acetic acid formation) and complete oxidation (CO_2 formation), which is particularly interesting for practical applications. Preliminary results of this study were published recently [38].

In the following we will, after a brief description of the experimental set-up and procedures (Section 2), first present and discuss results of potentiodynamic (Section 3.1) and potentiostatic (Section 3.2) measurements in 0.1 M and 0.01 M ethanol solutions, covering the wide temperature range between ambient temperature and 100 °C. The data are used to evaluate the current efficiency for the complete oxidation of ethanol to CO_2 under different conditions, and to calculate the apparent activation energies for the overall ethanol oxidation and for complete oxidation to CO_2 at different potentials (Section 3.3). Finally, the mechanistic and kinetic implications arising from these data as well as the importance of realistic reaction conditions in model studies for the prediction of the reaction behavior in fuel cells will be discussed.

2. Experimental

2.1. Elevated temperature DEMS set-up and experimental details

The DEMS set-up consists of the actual DEMS flow cell assembly, a differentially pumped two-chamber ultrahigh vacuum (UHV) system with a Balzers QMS 112 quadrupole mass spectrometer, a Pine Instruments potentiostat (model AFRDE5) and a computerized data acquisition system and had been described in more detail previously [38,39].

The DEMS flow cell assembly consisted of an electrochemical thin-layer flow cell, which was placed in a home-built air thermostat, and a second thin-layer compartment, which was connected to the electrochemical cell by an inert capillary and to the UHV system containing the mass spectrometer. A thin Teflon membrane (10 μm thick), supported on a stainless steel frit, separated the second compartment from the UHV. The electrolyte was supplied from pressurized glass bottles thermostated separately in two commercial thermostats (Lauda E200), the electrolyte flow was controlled by a pressure-resistant syringe pump (Harward Apparatus 11plus) connected to the outlet of the second flow compartment. The time delay between the onset in the production of gaseous species and their mass spectrometric detection (∼4 s at a flow rate of 15 $\mu L\,s^{-1}$), caused by the finite time required for the electrolyte to flow from the first to the second (detector) compartment, was corrected for accordingly.

The electrochemical thin-layer channel flow cell had been described and characterized in terms of its mass transport recently [35,38]. A Pt wire serving as counter electrode was placed in a separate compartment in the cell body, behind a glass frit in a circular opening directly in front of the working electrode. An external saturated calomel electrode (SCE), kept at ambient temperature, was used as a reference. All potentials, however, are quoted against that of a reversible hydrogen electrode (RHE). The potential with respect to the saturated calomel electrode was corrected to that of a reversible hydrogen electrode (RHE) reference at the respective reaction temperatures by measuring the onset of the HOR/HER on the same Pt/Vulcan catalyst thin film electrode at various temperatures under a constant hydrogen overpressure of 3 bar.

The circular thin-film Pt/Vulcan (20 wt% metal, E-TEK Inc.) electrode was prepared following the procedure described in ref. [40], by pipetting and drying 20 μL of an ultrasonically re-dispersed aqueous catalyst suspension (2 $mg\,mL^{-1}$) and then 20 μL of aqueous Nafion solution in the center of the mirror-polished planar glassy carbon rectangular plate (Sigradur G from Hochtemperatur Werkstoffe GmbH, 30 mm × 20 mm × 6 mm). This plate was mounted on the flow cell body. The resulting thin catalyst film had a diameter of ca. 5 mm, a geometric surface area of 0.2 cm^2, and a Pt loading of 40 $\mu g_{Pt}\,cm^{-2}$.

Before each measurement, the cell was carefully flushed with supporting electrolyte, then the thin-film electrode was cycled in the potential range between 0.06 and 1.16 V (100 $mV\,s^{-1}$ scan rate), until the cyclic voltammogram of a clean Pt/C electrode was reproduced [39]. The H_{upd} charge was used as an inherent reference to check for possible losses of catalyst after each experiment.

The supporting electrolyte was prepared using Millipore MilliQ water and suprapure sulfuric acid (Merck, suprapur). Ethanol (LiChrosolv) and formic acid (GR) were obtained from Merck. Before the measurements, all solutions were deaerated by high-purity Ar (MTI Gase, N6.0). All experiments were carried out at an overpressure of 3 bar and at temperatures between 23 and 100 °C, as indicated.

2.2. Calibration of elevated temperature and pressure DEMS set-up

The use of a non-porous Teflon membrane with low permeability, which was required to keep the water vapor level at tolerable levels at high temperatures and elevated pressure, also inhibits the permeation of larger molecules such as acetaldehyde. This allows us to monitor the CO_2 partial pressure via the $m/z = 44$ signal, without interference with the acetaldehyde signal at $m/z = 44$. The