



Electrooxidation of ethanol on Pt-based and Pd-based catalysts in alkaline electrolyte under fuel cell relevant reaction and transport conditions

S. Sun, Z. Jusys, R.J. Behm*

Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

HIGHLIGHTS

- ▶ Ethanol electrooxidation in alkaline solution was studied under fuel cell relevant conditions.
- ▶ Pt/C, PtRu black, Pd/C and Pd/CeO₂/C catalysts were used.
- ▶ Monometallic catalysts show better activities at high temperature and potential.
- ▶ Addition of oxophilic components is beneficial only for lower potentials.
- ▶ Effective activation energies are derived under steady-state conditions.

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ABSTRACT

Aiming at a detailed kinetic understanding under fuel cell relevant, but nevertheless well-defined reaction and transport conditions, the electrooxidation of ethanol on Pt-based (Pt/C, PtRu black) and Pd-based (Pd/C, Pd/CeO₂/C) catalysts in alkaline solution was investigated at temperatures up to 100 °C and at controlled electrolyte flow in a high temperature/high pressure thin-layer flow cell. Most important, the data reveal drastic effects of the reaction temperature. The apparent activation energies for ethanol oxidation on the different catalysts were determined and found to vary significantly with potential and the catalyst used. The addition of Ru to Pt and CeO₂ to Pd/C improves the tolerance toward catalyst poisoning at low potentials, while for higher potentials and especially at higher temperatures the activity of the monometallic catalysts is higher. For reaction at 0.5 V and 80 °C, the Pd/C catalyst exhibits the highest activity, both in terms of metal mass specific and active surface area normalized rates; the addition of an oxophilic component is beneficial only for lower potentials. Overall, the results illustrate the need for model studies under close to realistic reaction conditions for the understanding of reactions in fuel cells.

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1. Introduction

The electrooxidation of ethanol has attracted significant interest, both from fundamental reasons, as a model reaction for the electrooxidation of small organic molecules, and because of its potential application in direct ethanol fuel cells [1–6]. For reaction in acidic electrolyte, where most of the studies focused on, it was found that the reaction is kinetically hindered and requires a significant overpotential. Furthermore, efficient catalysis requires expensive noble metal catalysts [7,8]. In acidic medium, platinum is often considered to be the best monometallic catalyst for oxidation

of hydrocarbon molecules with its characteristic ability for catalytic C–H bond cleavage, whereas CO_{ad} oxidation on Pt electrodes requires a significant overpotential [5,9]. This is different for reaction in alkaline electrolyte, where overpotentials were found to be significantly lower and where inexpensive transition metal electrodes such as Ni and/or Ru were found to be highly active [10]. Recently, the interest in alkaline ethanol oxidation has been raised considerably by new developments in alkaline anion exchange membranes, which make alkaline ethanol oxidation fuel cells more feasible [11–14], and much of the research was addressed to transition metal electrodes, such as Ni, Au, Ag, Cu, Ru, Zn (also their combination with Pd or Pt) [10,15].

In the present paper, we report results of a comparative study on the EOR kinetics on three different carbon supported catalysts

* Corresponding author. Tel.: +49 731 50 25451; fax: +49 731 50 25452.
 E-mail address: juergen.behm@uni-ulm.de (R.J. Behm).

(Pt/C, Pd/C and Pd/CeO₂/C) and an unsupported PtRu catalyst (PtRu black). Most important and different from earlier studies, the measurements were performed on structurally well-defined electrodes and at well-defined transport conditions, but under fuel cell relevant reaction conditions, at elevated temperatures, up to 100 °C, and pressure (3 bar overpressure) and under continuous controlled electrolyte transport, which allows direct comparison of the measured reaction kinetics with the reaction in a fuel cell.

Previous studies on the ethanol oxidation reaction (EOR) in alkaline solution on different types of Pt-based or Pd-based electrodes, performed mostly under strongly idealized reaction conditions or as less well-defined fuel cell measurements, had come to the following conclusions: For the EOR in alkaline electrolyte on different types of Pt-based electrodes/catalysts (single crystalline and polycrystalline (pc) platinum and platinum alloys, carbon supported platinum and platinum alloy catalysts), previous studies [16–22] revealed lower overpotentials for the removal of electrode poisoning species such as CO_{ad} than in acidic electrolyte, due to the higher concentration of hydroxyl species [23]. Lai et al. [19,21] reported a considerable enhancement of the EOR activity on a pc platinum electrode in 0.1 M NaOH solution ethanol as well as a negative shift of about 100 mV in the onset potential (~50 mV in peak potential) compared to that in 0.1 M HClO₄ solution for similar ethanol concentration (0.5 M). Jiang et al. [20] determined an increase of the EOR current density on a Pt/C catalyst by factors of 4 (at 0.5 V vs. RHE) or 5 (at 0.6 V vs. RHE) in 0.1 M NaOH solution compared with those in 0.5 M H₂SO₄ solution (both cases 0.01 M ethanol) at room temperature, connected with a cathodic shift of the onset potential by about 80 mV. The addition of Sn to a Pt/C (PtSn/C) catalyst showed a negligible improvement in the EOR kinetics compared with that of a Pt/C catalyst in alkaline solution, in contrast to findings in acidic solution, where bimetallic PtSn catalysts are considered as most active catalysts [7,8,24–26]. A similarly small difference was observed also for a Pt₂Ru₃ catalyst, compared to a Pt/C catalyst, in the MOR kinetics in alkaline solution [27]. Also the product distribution in the EOR was much more favorable in alkaline than in acidic electrolyte. Rao et al. [17], who quantitatively determined the product distribution in a direct ethanol oxidation fuel cell by online mass spectrometry measurements, reported CO₂ current efficiencies in the order of 55% at a potential of 0.8 V vs. RHE on a Pt electrode (60 °C, 0.1 M EtOH in 0.2 M KOH), which is significantly higher than the CO₂ current efficiencies obtained in acidic media under similar conditions [17,28].

Palladium is known as a poor electrocatalyst for alcohol oxidation in acidic medium, but shows a remarkable EOR activity in alkaline environment [22,29–38]. Zheng et al. [39] investigated the activity of Pd catalysts, employing different types of support, and compared it with that of a Pt/C catalyst (in 1 M KOH + 1 M EtOH). They found that a multiwall carbon nanotube (MWCNT) supported Pd catalyst exhibited a higher activity, by a factor of 3, than the Pt/C catalyst. In order to improve the electrocatalytic activity and stability, oxide supports such as CeO₂ were added to the Pd/C catalyst [40], which increased the EOR activity in 1 M KOH containing 1 M ethanol compared to that of the pure Pd/C catalyst [33,40].

In the following, we will first briefly describe the setup used for these measurements and the experimental procedures. Next, we will present and discuss results on pre-adsorbed CO oxidation (Section 3.1), followed by potentiodynamic (Section 3.2) and potentiostatic (Section 3.3) measurements in 0.5 M NaOH. We will compare the mass specific and active surface area specific activities of the respective electrodes in the temperature range between 23 °C and 80 or 100 °C, respectively, at different potentials (Section 3.4). Apparent activation energies for ethanol oxidation reaction in alkaline solution on the Pt- and Pd-based catalysts were derived under similar reaction condition and discussed in the last part (Section 3.5).

2. Experimental

2.1. High temperature/high pressure flow cell setup

The high temperature/high pressure thin-layer channel flow cell [41] with well-defined mass transport characteristics used in this study is shown in Fig. 1. A Pt wire located in a separate compartment served as a counter electrode, an external saturated calomel electrode (SCE) kept at ambient temperature was used as a reference electrode (for details see Ref. [41]). All potentials, however, are quoted against those of a reversible hydrogen electrode (RHE) at the respective reaction temperature, which were determined in separate hydrogen evolution/oxidation experiments in H₂-saturated supporting electrolyte at each temperature [41]. The cell was located in an air thermostat and connected to a pressure-resistant syringe pump (Harward Apparatus 11plus), which controlled the electrolyte flow rate, and the pressurized glass bottles for electrolyte supply. The latter were thermostated separately in thermostats (Lauda E200). Connections were made from PEEK capillaries. The electrolyte was pressurized after purging with high purity N₂.

2.2. Electrode preparation

The circular thin-film catalyst electrodes (diameter ca. 5 mm, accessible geometric surface area 0.2 cm²) were prepared from commercial Pt/C (20 wt.% Pt, E-TEK Inc.); Pd/C (5 wt.% Pd, Degussa.); Pd/CeO₂/C (10 wt.% Pd, Hypermec Acta.); PtRu black (atomic ratio Pt:Ru = 1:1, Johnson Matthey) catalysts via the procedure described in Ref. [42], by pipetting and drying 20 μl of an ultrasonically re-dispersed aqueous catalyst suspension, and then 20 μl of aqueous Nafion solution, in the center of the mirror-polished rectangular glassy carbon plate (Sigradur G from Hochtemperatur Werkstoffe GmbH, 30 mm × 20 mm × 6 mm). This plate was mounted on the flow cell body (machined from PEEK) and pressed against a gasket with a pre-cut channel (for details see Ref. [41]). The resulting metal loadings were 10 μg_{Pt} cm⁻² for Pt/C, 40 μg_{Pd} cm⁻² for Pd/C, 40 μg_{Pd} cm⁻² for Pd/CeO₂/C, and 100 μg_(PtRu) cm⁻² for PtRu black. The corresponding mass specific

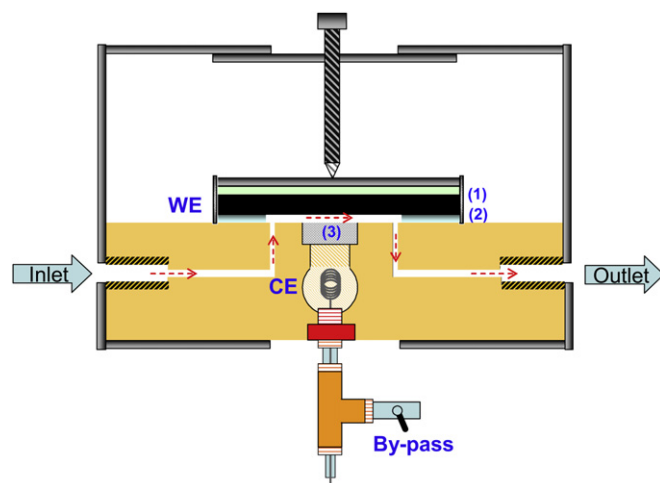


Fig. 1. Schematic drawing of the electrochemical high temperature/high pressure (HT/Hp) thin-layer channel flow cell: (1) working electrode (WE), (2) gasket, (3) porous glass frit. The reference electrode (saturated calomel electrode, SCE) is connected at the inlet of the cell via a Luggin capillary. A by-pass for the electrolyte helps to remove the gas bubbles formed at the counter electrode. The electrolyte flow is depicted by the arrows (from inlet to outlet).

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