



Investigation of ruthenium promoted palladium catalysts for methanol electrooxidation in alkaline media



Tilman Jurzinsky*, Patricia Kammerer, Carsten Cremers, Karsten Pinkwart, Jens Tübke

Fraunhofer Institute for Chemical Technology ICT, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany

HIGHLIGHTS

- Synthesis and physical evaluation of Ru containing Pd-based electrocatalysts.
- High electrocatalytic activity towards methanol oxidation for Pd₃Ru/C.
- Investigations on oxidative removal of CO on Pd, Ru and bimetallic catalyst surface.
- CO₂ current efficiency significantly enhanced by addition of Ru to Pd.
- Power density of 0.1 W cm⁻² for platinum-free alkaline direct methanol fuel cell.

ARTICLE INFO

Article history:

Received 17 August 2015

Received in revised form

14 October 2015

Accepted 2 November 2015

Available online 13 November 2015

Keywords:

Electrocatalysis

Alkaline

Methanol oxidation reaction

DMFC

CO₂ current efficiency

DEMS

ABSTRACT

In this study, the investigation of binary palladium based electrocatalysts for methanol oxidation in alkaline media is reported. For this purpose, electrocatalysts with a loading of 20wt% metal on VulcanXC72-R were synthesized via wet chemical reduction with various compositions of palladium and ruthenium. Physical characterization via transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and inductively coupled plasma optical emission spectroscopy (ICP-OES) was done and verified the synthesis of nanoparticles on carbon support. Electrochemical evaluation of the catalytic behavior of Pd/C, Ru/C and Pd_xRu/C (X = 1, 3, 5) via cyclic voltammetry and chronoamperometry was conducted in a 3-electrode setup. These measurements suggested that Pd₃Ru/C is a promising material for methanol oxidation reaction in alkaline media with an onset potential of 0.465 V_{RHE} and a peak current density of over 1 A mg⁻¹_{Pd}. To further investigate the oxidation of methanol on Pd/C and Ru promoted catalysts, differential electrochemical mass spectrometry (DEMS) measurements were done. From these results a higher CO₂ current efficiency (CCE) of 86% for Pd₃Ru/C compared to 65% for Pd/C was found. Moreover, fuel cell tests verified the results and showed that Pd₃Ru/C has the better performance.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Electrocatalytic oxidation of methanol (CH₃OH) was investigated intensively in the past decades especially. At first, the catalytic activity in acidic media was in focus because progress in proton-exchange membranes (PEMs) science made direct methanol fuel cells (DMFCs), which convert the chemical energy stored in methanol directly into electric energy, feasible. In this type of fuel cell, methanol is oxidized at the anode via numerous intermediate steps while at the cathode oxygen is reduced. DMFCs have certain advantages over conventional hydrogen driven fuel cells.

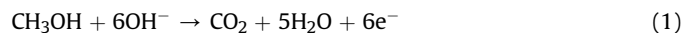
For example, the volumetric energy density of methanol is significantly higher than for liquefied hydrogen [1]. Besides this, working with methanol as fuel results in simple and easy to handle fuel cell systems. Even though methanol is toxic, it is favorable to use it in fuel cells because it is easy to store and already has an existing infrastructure for methanol storage, since it is used as reactant or solvent in the chemical industry [2]. Also, methanol is efficiently converted to CO₂ by Pt/C catalyst with a CO₂ current efficiency (CCE) of up to 90% in acidic media [3]. On the downside, DMFC power units which got commercialized in recent years by companies like SFC Energy AG (Brunnthal, Germany), IRD Fuel Cells (Odense, Denmark) or Oorja Fuel Cells (Fremont, California, USA) are still a niche product for portable back-up power or materials handling applications due to high costs for Pt-based catalysts [4,5].

A possible way to substitute the costly platinum in DMFC is to

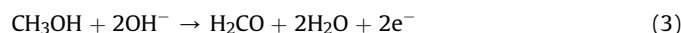
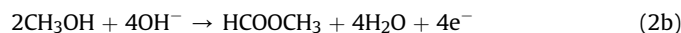
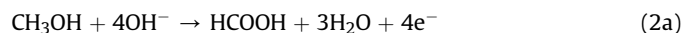
* Corresponding author.

E-mail address: tilman.jurzinsky@ict.fraunhofer.de (T. Jurzinsky).

switch from acidic to alkaline working conditions in the fuel cell as the kinetics of methanol oxidation reaction (MOR) are enormously enhanced in alkaline media and the use of other catalysts than Pt get feasible for MOR [6]. Like in acidic media, methanol is converted to CO₂ in several steps in alkaline media:



Beden et al. investigated the complex mechanism of MOR in alkaline media on a Pt electrode. It was shown that methanol is adsorbed on the platinum surface and is gradually oxidized via dehydrogenation of adsorbed CH_xO (X = 1, 2 or 3) reaction intermediates. While these reactions are considered to be fast and irreversible, the reaction of adsorbed CO with adsorbed OH on the platinum surface was postulated to be much slower making it the rate determining step [7]. Even though it is a reaction intermediate, adsorbed CO is often considered to be a catalyst poison as it is strongly bound to the catalyst surface and is only oxidized if it is able to react with nearby adsorbed OH. Several studies led to a deeper understanding of the MOR in alkaline media resulting in complex mechanism with 3 possible products during MOR: CO₂, formic acid and formaldehyde [8–12]. Usually, it is assumed that methyl formate (HCOOCH₃) is a product of the reaction between methanol and formic acid, which originates from MOR [13–15]. In a recent study, Abd-El-Latif and Baltruschat evidenced by studying the time constant for methyl formate formation in a DEMS flow cell that methyl formate is formed during oxidation of methanol at the catalyst surface via a nucleophilic attack of methanol on adsorbed methanol dehydrogenation species [16]. While the oxidation to CO₂ produces 6 electrons (Eq. (1)), the reactions leading to formic acid (Eq. (2a)), methyl formate (Eq. (2b)) or formaldehyde (Eq. (3)) produce fewer electrons per oxidized methanol molecule and are therefore less energy-efficient.



As a consequence, capable catalysts for MOR in alkaline media should be able to reach high CO₂ current efficiency (CCE) while undergoing low poisoning effects.

Palladium was proven to be a good alternative to Pt for alcohol electrooxidation in alkaline media [17–19]. Also, it was indicated that Pd inherits the same reaction mechanisms as Pt for alcohol oxidation reaction [20]. Xu et al. as well as Bayer et al. showed that Pd is even more catalytic active for ethanol oxidation reaction than Pt in alkaline media [17,21]. However, in the study by Xu et al. it was also evidenced that for methanol oxidation reaction Pt is still the more active catalyst. Therefore, Palladium-based catalysts were improved for methanol oxidation reaction by several research groups to compete with Pt. Most prominent examples are oxide promoted or bimetallic catalysts [22–32]. As it is known from DMFCs, Ru is likely to promote platinum in its ability to oxidize methanol by two main effects. Firstly, Ru is activating water at lower potentials and therefore forms oxide species on its surface at lower potentials than Pt. These oxygen-species on Ru are supporting the dehydrogenation and oxidation processes of adsorbed methanol species or CO on neighboring Pt sites [33–36]. Secondly, Ru modifies the electronic structure of the Pt surface, which results in a weakened Pt–CO bond strength [37–39].

In alkaline media PdRu/C catalysts were found to inherit significantly increased electrocatalytic activity towards the oxidation of several alcohols [40–42]. For ethanol, Ma et al. were able to

reach a power density of 176 mW cm⁻² at 80 °C in a AEM based direct ethanol fuel cell with Pd₃Ru/C anode catalyst [43]. Nevertheless, PdRu/C catalysts were neither investigated towards the ideal Pd:Ru ratio for methanol oxidation nor towards the influence of Ru on the MOR mechanism in alkaline media. In this study, we investigated on in-house made Pd_xRu/C (X = 1, 3, 5) catalysts and their activity towards methanol oxidation in dependency of Ru content. Firstly, physical characterization was done to evaluate the composition, morphology and particle size of the catalyst. Secondly, standard electrochemical tests like cyclic voltammetry (CV) and chronoamperometry (CA) in a stationary electrolyte cell were done to evaluate the activity towards MOR for these catalysts. Thirdly, CO stripping and CV experiments in a DEMS flow cell were conducted to further understand the synergistic effects of Pd_xRu/C and how Ru influences the product distribution during methanol oxidation. Finally, single cell tests showed whether Pd_xRu/C catalysts are of potential use in alkaline direct methanol fuel cell (ADMFC) applications.

2. Experimental

2.1. Electrocatalyst synthesis

All electrocatalysts were synthesized via wet chemical reduction of the metal salts in presence of a carbon support material (Vulcan[®] XC72R, Cabot Corporation). In a former study, we successfully used this synthesis method to form Pd_xNi/C or Pd_xAg/C catalysts [32]. As follows, the production of 1 g Pd₃Ru/C with a loading of 20 wt% active material is described.

In a 500 ml flask 800 mg of Vulcan[®] XC72R was weight in. In a second 500 ml beaker 250 mg PdCl₂ (1.4 mmol; 99%, Sigma Aldrich), 103 mg RuCl₃ (0.5 mmol; Sigma Aldrich), 4330 mg sodium citrate (20 mmol; p.a., Fluka) and 250 ml deionized H₂O were mixed together and stirred for 30 min. Sodium citrate was used as a stabilizing agent as it is suggested by other studies to prevent agglomeration of particles formed during reduction. Therefore the usage of sodium citrate leads to smaller catalyst particles than without it [44]. The mixture was added to the flask with the carbon support and sealed. To disperse Vulcan[®] XC72R the mixture was sonicated for 30 min with an ice-cooled Emmi[®]-60HC ultrasonic bath (EMAG AG). During this procedure, Argon was bubbled through the mixture to enhance the dispersion process. After sonication, the dispersion was stirred strongly and a freshly prepared 3 wt% sodium borohydride solution (300 mg in 10 ml H₂O, 7.9 mmol; 98%, Sigma Aldrich) was added slowly to the mixture. The dispersion was stirred for additional 30 min. The resulting carbon supported catalyst was separated from the dispersion by filtration, washed several times and dried in the fume hood at room temperature over night.

2.2. Physical characterization

All catalysts were investigated on their metal loading on carbon support and elemental composition by the following procedure. At first, thermogravimetric analysis (TGA) was conducted with TGA 2950 (TA instruments) in the temperature range 30–700 °C with a heating rate of 10 °C min⁻¹ in air atmosphere in order to find the metal loading on carbon. The metallic residue from TGA was dissolved with freshly prepared aqua regia (HCl:HNO₃ = 3:1). Following inductively coupled plasma optical emission spectroscopy (ICP-OES) on an iCAP 6300 ICP Spectrometer (Thermo Fisher Scientific) was used to evaluate the elemental composition of the catalysts.

Data on morphology, crystallite size and particle size was collected by using X-ray diffraction (XRD) and transmission

Download English Version:

<https://daneshyari.com/en/article/1285721>

Download Persian Version:

<https://daneshyari.com/article/1285721>

[Daneshyari.com](https://daneshyari.com)