Short Communication

Methanol oxidation on PdRh/C electrocatalyst in alkaline media: Temperature and methanol concentration dependencies

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ABSTRACT

PdRh/C is a highly active electrocatalyst for methanol oxidation reaction in alkaline media. In this study, the methanol oxidation at PdRh/C was investigated electrochemically in half-cell experiments for various temperatures and various methanol concentrations in the electrolyte. The results obtained by these measurements were compared to the ones of Pd/C. Thus, new insights on how Rh influences the electrocatalytic activity of Pd were found. The apparent activation energies calculated from potentiostatic and potentiodynamic measurements show that the apparent activation energy of the methanol oxidation reaction on Rh-modified electrocatalysts is significantly lower than for Pd/C, which is attributed to the enhancement of CO_{ads} oxidation on PdRh/C due to the oxophilic character of Rh. By determining the apparent reaction orders at different oxidation potentials (0.5–0.8 V) it was shown that for both catalysts the CO_{ads} oxidation is the rate determining step at potentials <0.8 V, but for PdRh/C the contribution of methanol adsorption to the apparent reaction order is higher than for Pd/C, which is also attributed to the enhanced CO_{ads} oxidation on PdRh/C.

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1. Introduction

Anion-exchange membrane direct methanol fuel cells (AEM-DMFCs) are considered to be a suitable candidate as a portable or back-up power source. Thus, this kind of fuel cell was investigated intensively in recent years. As this technology is still in the stage of development, research related to this topic focus on new materials, operation conditions and system development [1–4]. Beside the research on membranes which is particular challenging as the alkaline electrolyte is an aggressive media for the membrane stability because hydroxide is a strong nucleophile [4], electrocatalysts for the complete oxidation of methanol to CO_2 are of major interest in the field of materials research. Here it was shown, that Palladium on carbon is able to replace the costly Pt/C anode catalyst normally used in direct methanol fuel cells for the alkaline environment [5]. To better compete with Pt, Pd was recently modified in several ways including alloying or mixing with other active materials [6–10], controlling the shape and particle size of the nanocatalyst [11,12] or using other catalyst supports than carbon black [13,14]. The complete oxidation of methanol leads to CO_2. If methanol is not completely oxidized, side products like formaldehyde or formate are produced. These side products lead to a lower faradaic efficiency as less electrons are transferred per methanol molecule compared to the case of CO_2 being the reaction product. The methanol oxidation mechanism in alkaline media was already under

investigation in the 1960s. Bagotzky et al. showed that the oxidation of adsorbed CO (CO_{ads}), which is a reaction intermediate, is the rate-determining step during the methanol oxidation [15]. Therefore, CO_{ads} is also often considered a catalyst poison. CO adsorbed on the catalyst surface is oxidized via a Langmuir-Hinshelwood-mechanism:

$$CO_{ads} + 2OH^- \rightarrow CO_2 + H_2O + 2\ e\text{-} \tag{1}$$

The oxidative removal of adsorbed carbon monoxide at low oxidation potentials plays a key role in developing efficient anode catalysts for AEM-DMFCs. The formation of adsorbed OH on the catalyst surface plays an important role in this process as well as in the dehydrogenation of adsorbed methanol species (CH_XO_{ads}, X = 1–3) [16,17]:

$$OH^- \rightarrow OH_{ads} + e\text{-} \tag{2}$$

$$CH_3OH_{bulk} \rightarrow CH_3OH_{ads} \tag{3}$$

$$CH_3OH_{ads} + 4OH^- \rightarrow CO_{ads} + 4H_2O + 4e\text{-} \tag{4}$$

Therefore, mixing oxophilic metals to Pd was proven to be beneficial for improving the activity towards methanol oxidation reaction (MOR) of Pd-based catalysts due to a bifunctional mechanism [6–8].

A promising candidate as catalyst for the electrochemical oxidation of methanol in alkaline media is PdRh/C. Due to its oxophilic character, Rh is able to promote Pd in its ability to oxidize methanol to CO_2 and suppress the production of unwanted side products from the reaction. Besides this, catalyst poisoning by adsorbed CO on the catalyst surface

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was also less severe for PdRh/C compared to Pd/C [7]. As it was also shown in the mentioned study that PdRh/C exhibits two catalytically active sites for methanol oxidation reaction with two oxidation peaks in cyclic voltammetry experiments, we herein present further work on the temperature dependence and apparent reaction order of this catalyst in comparison with Pd/C.

2. Experimental section

The synthesis, electrochemical and physical characterization of the herein investigated electrocatalysts is described elsewhere [7].

2.1. Materials

The chemicals used for catalyst ink preparation and electrochemical testing in this study were methanol (CH_3OH, p.a., Merck Millipore), ethanol (C_2H_5OH, p.a., Merck Millipore), 20 wt% PTFE dispersion and potassium hydroxide (KOH, TraceSELECT®, Sigma-Aldrich) and were used as received without any further purification. All solutions and inks were prepared with de-ionized water (with an ionic conductivity <55 nS cm^{-1}).

2.2. Electrode preparation

For electrochemical measurements catalyst inks were prepared by stirring 1.5 mg of catalyst with 31.7 μl ethanol for 24 h. Afterwards 5.5 μl of a 7.5 wt% PTFE dispersion was pipetted slowly to the mixture. The mixture was sonicated for 30 min (ice-cooled ultrasonic bath, Emmi®-60HC, EMAG AG). To conduct the measurements, 2 μl of the ink was pipetted onto a glassy carbon electrode (GCE, d = 5 μm, A = 0.196 cm^2) resulting in a thin, homogenous catalyst layer with a PTFE content of about 20 wt%.

2.3. Electrochemical testing

For temperature dependent measurements a mantled glass cell (Pine Instruments) was used. The temperature of the mantle compartment was held constant by using a GD 120 thermostat (Grant Instruments Ltd.) at 20.0, 27.5, 35.0, 42.5 and 50.0 °C. The temperature in the electrolyte was measured via a Type K thermocouple and was stable to a tolerance of ±0.2 °C. The 3-electrode setup consisted of a catalyst coated rotating disc electrode (RDE, diameter = 5 μm, area = 0.1962 cm^2), Pt wire and a Hydroflex® reversible hydrogen electrode (RHE, Gaskatel GmbH) as working, counter and reference electrode, respectively. Before the actual measurement, the working electrode was electrochemically cleaned and preconditioned by applying cyclic voltammetry (CV) between 0.1 and 1.2 V (vs. RHE) at a scan rate of 100 mV s^{-1} for 80 cycles in 0.1 M KOH electrolyte. After that the electrolyte was changed to a methanolic solution (0.1 M CH_3OH + 0.1 M KOH) and the wanted measurement temperature was adjusted and held stable for 30 min. At a constant temperature 20 cycles at 50 mV s^{-1} and 3 cycles at 20 mV s^{-1} were recorded in the same potential range without the RDE being rotated. Following chronoamperometric measurements were done at 400 rpm rotation speed and an oxidation potential of 0.7 V (vs. RHE) for 1000 s. From temperature dependent cyclic voltammograms at a scan rate of 20 mV s^{-1} and chronoamperometric measurements in the methanolic solution the apparent activation energy (E_a) of methanol oxidation reaction was calculated via Arrhenius equation according to the literature of Cohen et al. in dependence of the oxidation potential [18].

The determination of the apparent reaction order was done at potentials ranging from 0.5 to 0.8 V (vs. RHE) via chronoamperometry (CA) in electrolytes with different concentrations of methanol (0.05 M, 0.1 M, 0.5 M or 1.0 M) and 0.5 M KOH. The calculation of the reaction order was done according to the literature [19].

3. Results and discussion

3.1. Temperature-dependent measurements

Cyclic voltammograms and chronoamperometric curves for the methanol oxidation in alkaline media were recorded for Pd/C and PdRh/C in a temperature range from 20 to 50 °C. Resulting curves from CV are shown in Fig. 1. Compared to a former study on Pd/C and PdRh/C the curves obtained by CV show similar shapes [7]. In contrast to Pd/C, PdRh/C exhibits two separated methanol oxidation current peaks.

For Pd/C the methanol oxidation current is rising with increasing temperature. The onset potentials do not vary significantly with changes in temperature while the peak potentials slightly shift to higher potentials with rising temperature. Nevertheless, the shapes of the CV curves do not change with the temperature increase. These observations indicate that the methanol oxidation reaction mechanism on Pd/C keeps constant regardless of operation temperature in the tested temperature range, but that the reaction rate is changed. The apparent activation energy of methanol oxidation on Pd/C was calculated according to the literature [18] based on the peak currents and steady-state currents measured under potentiostatic conditions at 0.7 V, respectively. The obtained values are shown in Table 1.

Comparing the apparent activation energy values obtained with values in the literature is difficult as multiple factors like electrode preparation, electrolyte composition and studied potentials influence the energy values. Nevertheless, Wang et al. found values between 28.1 and 37.9 kJ mol^{-1} for methanol oxidation on Pd electrodes in 1 M KOH + 1 M CH_3OH electrolyte dependent from the applied potential [20]. As these values are in the same range as the ones shown herein,
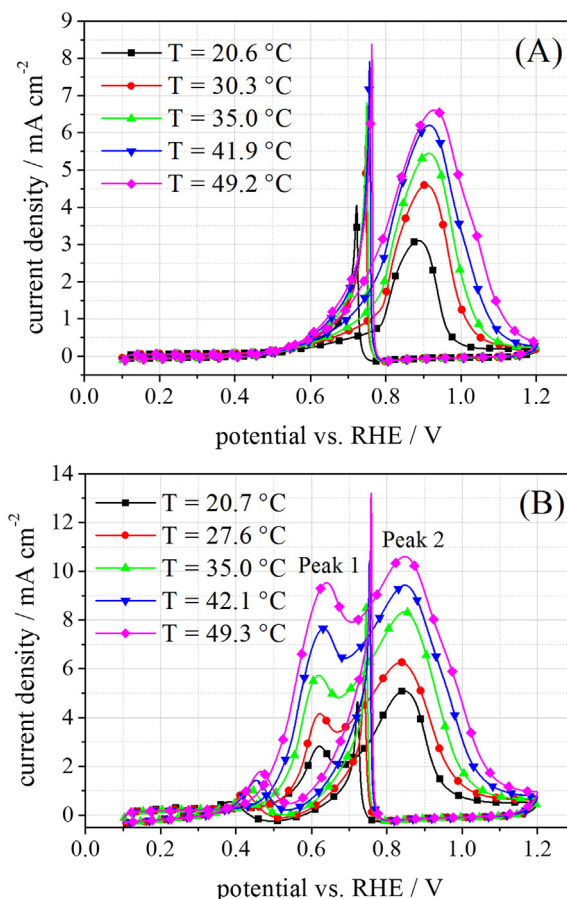

Fig. 1. Cyclic voltammetry curves for (A) Pd/C and (B) PdRh/C in 0.1 M KOH + 0.1 M CH_3OH electrolyte at a scan rate of 20 mV s^{-1} at various temperatures.