Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 52 (2007) 5606–5613

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

The use of CO stripping for in situ fuel cell catalyst characterization

Tanja Vidaković [a,*], Mihai Christov [a,b], Kai Sundmacher [a,c]

[a] *Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstr. 1, D-39106 Magdeburg, Germany*
[b] *University of Chemical Technology and Metallurgy, Department of Physical Chemistry, 1756 Sofia, Bulgaria*
[c] *Otto-von-Guericke-University Magdeburg, Process Systems Engineering, Universitätsplatz 2, D-39106 Magdeburg, Germany*

Received 10 October 2006; received in revised form 16 December 2006; accepted 16 December 2006
Available online 23 January 2007

Abstract

An important parameter in normalizing activities of porous electrocatalysts is real surface area of the catalyst. In this study CO stripping voltammetry was applied for the determination of the surface area of PtRu catalysts in a membrane electrode assembly. The difficulties in applying this method are summarized and a practical solution for the "accurate" voltammetric CO charge determination is suggested. The influence of adsorption time, potential, sweeping range and sweep rate on voltammetric CO charge determination is studied. It is shown that the CO charge determined in this way is independent on the sweep rate applied.

Keywords: Surface area determination; CO stripping; Cyclic voltammetry; PtRu catalyst; Membrane electrode assembly (MEA)

1. Introduction

In electrochemistry, the term "real surface area" means the electrochemically active surface area under working conditions. For porous electrodes in fuel cells it refers to the surface area of metal particles, which are at the same time in contact with the electrolyte (in this case Nafion®) and the current collector (usually carbon cloth or carbon paper). From the fundamental point of view, determination of the real surface area is important in order to normalize activities of different electrocatalysts to the same number of reactive surface sites. From the more practical point of view the real surface area determination is important in order to check catalyst durability by measuring the loss of catalyst active surface area during fuel cell operation.

The real surface area under fuel cell conditions can be determined by hydrogen adsorption method, but only in the case of Pt catalyst. The CO adsorption method is more promising in terms of its more general applicability, but its application is connected with many uncertainties. Some of them arise from unknown type of CO bonding on the surface [1]. The other uncertainty is connected with accurate CO stripping charge correction in respect to other contributions like double layer charging and charging due to metal oxide formation [2]. In the case of PtRu catalyst this problem is significant since oxide formation on PtRu catalyst overlaps with CO oxidation [3]. For this reason the CO voltammetric charge determination is usually used only in a qualitative way and stated that the surface area is only given (if it is given) as a relative and not absolute value.

It was shown recently that the CO charge can be accurately determined by using Infra-Red (IR) [4] or differential electrochemical mass spectroscopy (DEMS) [5]. These techniques have one major advantage compared to voltammetric CO charge determination, namely CO charge determined in this way is free from other faradaic and non-faradaic contributions. However there are some disadvantages, like applicability of these techniques in the fuel cell labs and on real catalyst and this issue is especially important in determining the loss of catalyst activity during fuel cell long term operation.

In this paper a practical solution for the "accurate" voltammetric CO charge determination is described. The influence of adsorption time, potential, sweeping range and sweep rate for real surface area determination of unsupported PtRu catalysts in a membrane electrode assembly (MEA) under fuel cell relevant conditions is studied. It is shown that the CO charge determined in this way is independent on the sweep rate applied. First, a system characterization with an unsupported Pt catalyst as a test system was carried out. Then the method is established by trying out different strategies for voltammetric CO stripping charge

---

[*] Corresponding author. Tel.: +49 391 6110 319; fax: +49 391 6110 553.
E-mail address: vidakovi@mpi-magdeburg.mpg.de (T. Vidaković).

0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.12.057

integration and base line subtraction. Finally the method is tested on the literature data [5] for CO stripping on PtRu catalyst in DEMS configuration and good agreement to CO charge recalculating from MS signal (which was free from other faradaic and non-faradaic contributions) is obtained.

2. Experimental

2.1. Cell

All electrochemical measurements were performed in a special electrochemical cell—cyclone flow cell (Fig. 1). This cell enables the investigation of the kinetics of electrochemical reactions under fuel cell relevant conditions at well-defined potential control conditions [6,7].

The working electrode compartment (1) was supplied with nitrogen or CO/Argon gas mixture, while the counter (2) and the reference electrode (3) compartments with 1 M sulphuric acid solution. Sulphuric acid container was de-aerated with nitrogen and circulated through the counter electrode compartment of the cell. The electrolyte solution was prepared from sulphuric acid (Merck, extra pure) and ultra pure water (Millipore, 18 MΩ cm). The reference electrode was a saturated silver/silver chloride (0.196 V versus SHE).

The experiments were performed at room temperature (22 ± 0.5 °C).

2.2. Working electrode—MEA preparation

Unsupported PtRu (HiSpec 6000) and Pt Johnson Matthey catalysts were used. In the case of PtRu catalyst Pt:Ru atomic ratio was 1:1. The total metal loading for both Pt and PtRu catalysts was 5 mg cm^{-2}. Catalyst ink was prepared by suspending a proper amount of catalyst powder in ultra pure water (Millipore, 18 MΩ cm), with addition of aqueous Nafion® solution in water in order to obtain 15 wt% of Nafion® in the catalyst layer. The suspension was first agitated in an ultrasonic bath for 15 min and then additionally stirred for 3 days. Then the catalyst was sprayed only on one side of a Nafion® 105 membrane. The schematic representation of MEA is given in Fig. 1. Details about membrane pre-treatment are given in [8]. The back diffusion layer (BDL) was teflonised Toray® paper (type TGP-H-060). The Teflon content in the BDL was approximately 22 wt%. Details about Toray® paper pre-treatment are given in Ref. [9]. The MEA was prepared by hot pressing of the gas diffusion electrode (Nafion® membrane and catalyst layer) at 130 °C and at a pressure of 10 MPa during 3 min onto a teflonised BDL. The total geometric area of MEA was 12.56 cm^2, while the surface area directly exposed to the electrolyte was 2.14 cm^2. Some edge effect was encountered and in an independent measurement with a MEA of total geometric area of 2.14 cm^2 a factor of 1.51 was obtained. So in specific surface area calculations the value of 3.24 cm^2 for geometric surface area was taken.

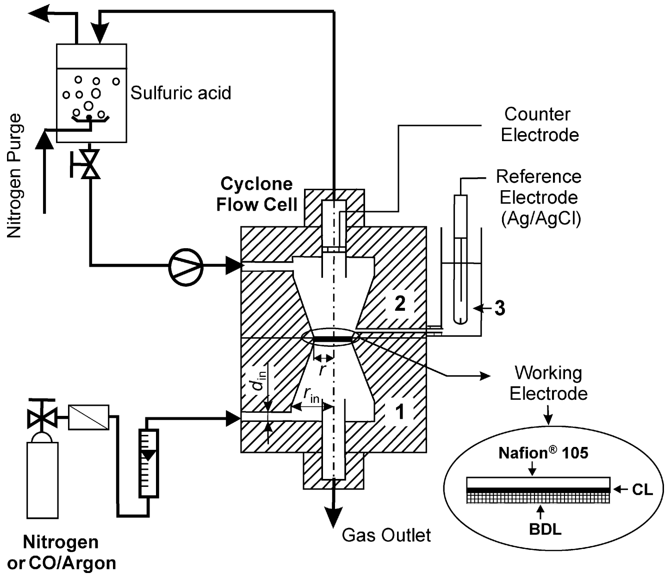

Fig. 1. Schematic representation of cyclone flow cell.

2.3. Electrochemical measurements

All electrochemical measurements were carried out with a Zahner impedance measurement unit (IM6e).

Preconditioning of the electrode was done by cyclic voltammetry in the potential range from −0.15 V to 0.5 V versus Ag/AgCl–PtRu electrode and −0.15 V to 1.2 V versus Ag/AgCl–Pt electrode, at a sweep rate of 20 mV s^{-1}. In the case of PtRu catalyst preconditioning is done in a more narrow potential limits, than for Pt catalyst, in order to avoid possible Ru dissolution [10]. This point is further commented in the section explaining influence of the potential range on CO stripping charge. During the preconditioning procedure N_2 was flowing through the working electrode compartment.

CO stripping. CO was adsorbed by flowing 0.1% CO in Argon (Technische Gase, Westfalen AG, Germany) at a flow rate of 140 ml min^{-1} through the working electrode compartment, for different adsorption times, while holding the electrode potential at constant value. By keeping the potential at the same value the gas was switched to N_2 for 30 min, in order to remove CO traces from the gas phase. After additional 30 min, the potential was scanned from the starting potential to 1.0 V and then back to 0.2 V.

In most of the experiments the CO adsorption potential was 0.0 V versus Ag/AgCl, and in some cases −0.1 V versus Ag/AgCl. Positive potential limit was also varied (from 0.45 V up to 1.05 V versus Ag/AgCl) and the sweep rate was varied from 5 mV s^{-1} to 50 mV s^{-1}.

The ohmic drop was compensated during all measurements using the ohmic resistance values estimated by prior impedance measurements. Typical resistance values under the experimental conditions in this work were 1.6 ± 0.3 Ω. The ohmic drop compensation during the measurement was 90% of the determined ohmic resistance value. The difference to 100% was corrected during data processing.

The mean particle size was determined by transmission electron microscopy (TEM) measurements. The CM200 instrument (Physical Department of Otto von Guericke University in Magdeburg) was used. The samples were prepared by ultrason-