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A rotating rod electrode disk as an alternative to the rotating disk electrode for medium-temperature electrolytes, Part II: An example of the application in an investigation of the oxygen reduction reaction on a Pt/C catalyst by the thin film method in hot concentrated H_3PO_4

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ABSTRACT

In this paper a novel and simple method to determine the O_2 reduction reaction activity of Pt/C in 99% H_3PO_4 at a temperature of 160 °C using a well-established thin film procedure is reported. It utilizes a disk of rotating rod made of glassy carbon as a working hydrodynamic electrode. By introducing polybenzimidazole as a thin film polymer binder, a modified rotating rod electrode disk (the cylindrical part is electrochemically inactive under the conditions used) suitable for measurements in hot concentrated H_3PO_4 was obtained. Using this electrode together with the Koutecky-Levich equation modified for rotating rod electrode hydrodynamics, the kinetics of the oxygen reduction reaction and mass transfer parameters of O_2 in 99% H_3PO_4 at 160 °C were successfully determined. The presented method can be easily used to determine the activity of various catalysts under conditions which preclude the use of a conventional rotating disk electrode.

1. Introduction

As a part of the hydrogen economy, fuel cells with a proton-exchange membrane represent a progressive solution for the transformation of the chemical energy in H_2 and O_2 into electricity [1]. Generally, two types of proton-exchange membrane fuel cells are recognized, the low temperature (LT PEM FC) and the high temperature (HT PEM FC) ones. Both types predominantly utilize catalysts based on Pt nanoparticles supported on carbon. The difference between them, however, is the operating temperature. Nafion®-type membranes limit the operating temperature of the LT PEM FC to below 90 °C. The HT PEM FC is operated at 120–200 °C. Consequently, a polybenzimidazole-type polymer (PBI) doped with H_3PO_4 has to be used as the proton-exchange membrane (PEM) [2,3]. H_3PO_4 leaks out of the membrane and is an indispensable part of the catalytic layer where it ensures the required proton conductivity. The higher temperature increases resistance to poisoning of the catalyst, especially by CO, and allows utilization of the waste heat. On the other hand, the presence of H_3PO_4 at an elevated temperature enhances degradation mechanisms such as agglomeration of Pt nanoparticles and Ostwald ripening or oxidation of the membrane and catalyst support [3–6]. H_3PO_4 negatively influences the electrochemically active surface area of a Pt catalyst, mainly due to the adsorption of $H_2PO_4^-$ anions [7–9]. The Pt catalyst is also affected by impurities present in H_3PO_4 or produced directly during HT PEM FC operation by H_3PO_4 electrochemical reduction and/or by chemical reduction by H_2 on Pt nanoparticles [10–12]. For example, H_3PO_3, as a representative of these impurities, was shown to strongly compete with electrolyte anions and adsorbed hydrogen for the available adsorption sites on a Pt surface and this effect increases with rising temperature [13]. In summary, all these effects negatively influence the rate of fuel cell reactions, especially the rate of the oxygen reduction reaction (ORR) [14–16].

To minimize the negative effects of the H_3PO_4 presence in the HT PEM FC, new Pt-based catalysts are being developed. The primary characterization of these Pt catalysts is focused on their morphology, chemical composition of alloys or composites and size of Pt nanoparticles [17]. Though useful from a structural point of view, such information cannot readily be linked to the actual

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List of symbols

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I	measured current (A)
I_k	kinetic current (A)
I_b	binder diffusion current (A)
I_{lim}	limiting electrolyte diffusion current (A)
δ_f	binder film thickness (m)
n	number of exchanged electrons (1)
F	Faraday constant (96 487 C mol^{-1}) (C mol^{-1})
A	geometric area of the disk (m^2)
$D_{i,b}$	diffusion coefficient of the electroactive specie *i* in the binder ($m^2\,s^{-1}$)
$c_{i,b}{}^*$	concentration of the electroactive specie *i* in the binder at the interphase with the electrolyte (mol m^{-3})
ν	kinematic viscosity of the electrolyte ($m^2\,s^{-1}$)
$D_{i,app}$	apparent diffusion coefficient of the electroactive specie *i* in the electrolyte ($m^2\,s^{-1}$)
$c_{i,e}{}^*$	bulk concentration of the electroactive specie *i* in the electrolyte (mol m^{-3})
$D_{i,b}\ c_{i,b}{}^*$	apparent diffusivity coefficient of the electroactive specie *i* in the binder (product of diffusion coefficient and concentration of electroactive specie in a binder at the interface with electrolyte) (mol $m^{-1}\,s^{-1}$)
ω	angular velocity (rad s^{-1})
δ	diffusion layer thickness (m)
$j_{0,app}$	apparent exchange current density (A m^{-2})
$E_{\log j=0}$	potential at log*j* = 0 in Tafel plot (*j* = 1 A m^{-2}) ((vs. MSE)/V)
α	charge transfer coefficient (1)
f	hydraulic correction factor in Koutecky-Levich equation for the RRE disk (*f* = 1.18) (1)

catalytic activity. Electrochemical methods, on the other hand, allow direct investigation of electrode reactions by means of, for instance, impedance spectroscopy and voltammetry [18,19].

To determine the electrochemical activity of the catalyst, the catalyst has to be in contact with the surface of the electron conductor. The most direct way is preparation of a gas-diffusion electrode with a catalyst layer and its subsequent characterization in a half-cell or in a fuel cell [20–24]. The disadvantages of this system are the very high capacitive currents and more importantly the rather complex nature/structure of the gas-diffusion electrode, which makes it difficult to interpret the obtained results. A more practical approach is to prepare a thin film layer of catalyst on an inert conductive material immobilized by a polymeric binder [25–29]. An alternative is to immobilize the catalyst in a defined cavity of a Pt microelectrode as described in the work of Guilminot et al. [30]. This is the only known method with no need of a catalyst binder, although a background ORR on Pt wire represents a major part of the experimental current response, not to mention the fact that a Pt microelectrode with a cavity would be prone to partial dissolution in the aggressive environment of hot concentrated H_3PO_4 [31].

The thin film method, especially in combination with a rotating disk electrode (RDE), is the most useful and versatile of all the methods listed. It enables voltammetry measurements to be performed with controlled hydrodynamics which are useful not only for the study of reaction kinetics, but also to determine the mass-transfer parameters of the electroactive species under practically steady state conditions. The diffusion coefficients of the electroactive specie *i* in both the electrolyte and the binder can be calculated by means of modified Koutecky-Levich analysis (Eq. (1)), as proposed by Lawson et al. [32] and used by numerous other authors [27–29,32]. The hydrodynamic conditions and flow pattern evolved around the modified RDE are more or less addressed by the proportionality factor of value 0.62.

$$\frac{1}{I}=\frac{1}{I_k}+\frac{1}{I_b}+\frac{1}{I_{lim}}=\frac{1}{I_k}+\frac{\delta_f}{nFAD_{i,b}c^*_{i,b}}+\frac{\nu^{1/6}}{0.62nFAD^{2/3}_{i,app}c^*_{i,e}\omega^{1/2}} \qquad (1)$$

I – measured current (A), I_k – kinetic current (A), I_b – binder diffusion current (A), I_{lim} – limiting electrolyte diffusion current (A), δ_f – binder film thickness (m), n – number of exchanged e^- per electroactive specie *i*, F – Faraday constant (96 487 C mol^{-1}), A – geometric area of the disk (m^2), $D_{i,b}$ – apparent diffusion coefficient of the electroactive specie *i* in the binder (m^2 s^{-1}), $c_{i,b}{}^*$ – concentration of the electroactive specie *i* in the binder at the interface with electrolyte (mol m^{-3}), ν – kinematic viscosity of the electrolyte (m^2 s^{-1}), $D_{i,app}$ – apparent diffusion coefficient of the electroactive specie *i* in the electrolyte in (m^2 s^{-1}), $c_{i,e}{}^*$ – bulk concentration of the electroactive specie *i* in the electrolyte in (mol m^{-3}), ω – angular velocity in (rad s^{-1}).

Eq. (1) for the thin-film modified RDE is subject to the following conditions: the binder film on the top of the catalyst is considered to be compact and uniform; the thin film itself should be homogeneous and cover the entire area of the disk. Roughness of the thin film on the disk surface can also affect the electrolyte flow and in turn the determined mass transfer parameters of the electro-active species. Appelquist et al. [33] presented a mathematical model describing this effect and concluded that defects of a characteristic dimension on a disk surface smaller than the thickness of the diffusion layer have no significant impact on the uniformity of electrolyte flow towards the rotating disk. On the other hand, a porous thin film with low roughness, but high thickness in the order of 0.1 mm could cause non-linear dependence of the limiting currents on the revolution rate [34,35]. I_k in the modified Koutecky-Levich equation for the RDE with thin film is also directly influenced by the size of the catalyst particles present in the thin film as well as by the homogeneity of their distribution [36,37]. In an optimal case I_k divided by the electrochemically active surface area (EASA) should be independent of catalyst loading. Any deviations from this fundamental condition signify a non-negligible influence of the catalyst support or simply insufficient precision of the thin film preparation [38].

In principle, the preparation of the thin film itself is quite straightforward. The catalyst is suspended in an appropriate solvent in the form of ink using ultrasonication and then a defined volume of this ink is deposited onto the disk. After drying, the catalyst is immobilized by a polymeric binder, usually a solution of Nafion® [26,28,29,38]. In order to increase adhesion of the thin film to the disk, in several studies the polymeric binder was added directly to the ink suspension before its deposition [25,38–40]. However, the rate of the ORR on such a thin film cannot be described by the modified Koutecky-Levich equation (Eq. (1)) mentioned since the binder probably does not form a uniform film on the top of the catalyst layer. Instead, the majority of the catalyst particles would be covered with the binder, resulting in a stronger influence of electroactive specie diffusion through the polymer. Additionally, it is very likely that some of the catalyst particles covered by the Nafion shell would not have any electronic contact with the electrode surface. The main weakness of the thin-film method is the non-homogeneous distribution of the catalyst on the disk. During the application of the ink on the disk surface the catalyst particles agglomerate near its edges, thus creating the so-called “coffee ring” effect. Studies by Ke et al. and Garsany et al.