



A rotating rod electrode disk as an alternative to the rotating disk electrode for medium-temperature electrolytes, Part I: The effect of the absence of cylindrical insulation



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ABSTRACT

In this paper, a rotating rod electrode disk is introduced as a hydrodynamic electrode and both the electrolyte flow hydrodynamics as well as mass transport towards the disk were investigated and compared with the rotating disk electrode. The main difference to the rotating disk is the absence of disk insulation leading to slightly enhanced mass transport towards the disk surface. Based on a combination of experiments and mathematical modelling for a broad range of kinematic viscosity values of the electrolyte solution, a correction of the Levich equation was introduced. This enables recalculation of the data determined using the rotating rod disk electrode so that they are equivalent to those of the rotating disk electrode. Although glassy carbon was used as the material of the rotating rod electrode in this work, in principle any other suitable material can be used. Thus, it can be concluded that the rotating rod electrode disk represents a cheap and effective tool easily applicable for measurements with controlled electrolyte convection in systems that are hardly manageable using a conventionally constructed rotating disk electrode. Good examples are melts or electrolyte solutions at temperatures above 80 °C. The applicability of the rotating rod electrode disk was successfully tested in the continuation (Part II) of this study. There, the thin-film modified (activated) rotating rod electrode disk was used for determining the mass transport properties of the oxygen and kinetic constants of the oxygen reduction reaction in concentrated phosphoric acid at 160 °C.

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1. Introduction

A rotating disk electrode (RDE) is a powerful tool in electrochemistry and electroanalytical chemistry. It is useful for performing a variety of measurements under controlled electrolyte flow dynamics along the electrode surface. This is highly beneficial for the determination of the electrode kinetics as well as the diffusion coefficients of electroactive species under steady state conditions. The main advantages of the RDE are the ability to control the diffusion layer thickness near the electrode and rapid attainment of steady state at the electrode [1,2]. Although a chronocoulometry at a stationary electrode can be used as a complementary method to the RDE technique for determination of mass transfer and kinetic parameters, the current response, in the case of chronocoulometry, is much lower due to the absence of forced convection. Furthermore its time-dependence makes the

data analysis more complex [1,3]. Using the RDE technique, the diffusion coefficient of electroactive species in the electrolyte solution can be determined using the Levich equation (Eq. (1)).

$$j_{\text{lim}} = \frac{I_{\text{lim}}}{A} = 0.62nFD^{2/3}c^*\nu^{-1/6}\omega^{1/2} \quad (1)$$

I_{lim} – limiting current (A), j_{lim} – average limiting current density (A m^{-2}), n – number of exchanged e^- per electroactive specie, F – Faraday constant (96487 C mol^{-1}), A – geometric area of the electrode disk (m^2), ν – kinematic viscosity of the electrolyte ($\text{m}^2 \text{ s}^{-1}$), D – diffusion coefficient of the electroactive species in the electrolyte solution/melt ($\text{m}^2 \text{ s}^{-1}$), c^* – bulk concentration of the electroactive species in the electrolyte solution/melt (mol m^{-3}), ω – angular velocity (rad s^{-1}) is calculated from revolution rate rev (RPM), according to Eq. (2).

$$\omega = \frac{2\pi \cdot rev}{60} \quad (2)$$

A value of 0.62 in the Levich equation (Eq. (1)) represents a proportionality factor which partially addresses the velocity

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Nomenclature

List of symbols

I	measured current A
I_k	kinetic current A
I_{lim}	limiting current A
n	number of e^- exchanged per electroactive specie 1
F	Faraday constant (96 487 C mol ⁻¹) C mol ⁻¹
A	geometric area of the disk m ²
D	diffusion coefficient of the electroactive species in the electrolyte m ² s ⁻¹
ν	kinematic viscosity of the electrolyte m ² s ⁻¹
c^*	bulk concentration of the electroactive species in the electrolyte mol m ⁻³
c	concentration mol m ⁻³
ω	angular velocity rad s ⁻¹
Re	Reynolds criterion 1
R	total diameter of RDE (including insulation) m
\mathbf{v}	velocity vector m s ⁻¹
ρ	mass density kg m ⁻³
μ	dynamic viscosity Pa s
p	static pressure Pa
j_{lim}	average limiting current density A m ⁻²
$j_{lim,loc}$	local limiting current density A m ⁻²
$j_{0,app}$	apparent exchange current density A m ⁻²
\mathbf{J}	molar flux vector mol s ⁻¹ m ⁻²
α	charge transfer coefficient 1
β	symmetry factor 1
f	correction hydraulic factor in Levich equation for RRE disk 1
w	mass fraction %
v_r	radial flow velocity
v_z	normal flow velocity

distribution perpendicular to the disk surface in its near vicinity. In other words, the value includes the effect of the thickness of the hydrodynamic Prandtl layer [1].

In real systems, several factors can affect current densities recorded using the RDE. The first and most important one is the construction of the RDE itself. Commercial rotating electrodes are made of an active part, the disk, and insulation around the disk edges whose thickness usually exceeds the diameter of the disk. The insulation has multiple functions: (i) it effectively defines the geometric electrode area and (ii) ensures a homogeneous fluid flow character at the edge of the disk [2]. One of the assumptions made when deriving the Levich equation (Eq. (1)) is the absence of any rotating disk boundaries. This condition cannot be fulfilled in real systems, but a RDE with non-conductive insulation of sufficient thickness around the disk closely approaches this ideal case. The most common form of insulation is a simple cylinder. Such a form exhibits a deviation of around 3% compared to the theoretical limiting current calculated from the Levich equation. According to Azim and Riddiford, the deviation can be reduced to approximately 1% by modifying the shape of the insulation [4]. It is evident that the axis of rotation of the RDE has to perfectly coincide with the centre of symmetry of the RDE. As described in the work of Mohr et al., even a small eccentricity increases the mass transfer rate towards the disk surface [5]. If the RDE does not meet the requirements listed above, the limiting current obtained deviates greatly from that calculated by the Levich equation. In an ideal case, the flow around the RDE surface is laminar [6,7]. The Reynolds criterion determines the character of the flow parallel to the RDE

surface for the RDE geometry (Eq. (3)).

$$Re = \frac{\omega R^2}{\nu} \quad (3)$$

R – diameter of the RDE, including cylindrical insulation (m)

For the majority of RDE systems a useful range of revolution rates is 100–10 000 RPM. The upper limit is given by the Reynolds criterion, determining the maximum value of ω at which the flow is still laminar. The lower limit of ω is given by the approximation used in the Levich equation, namely by the condition of hydrodynamic boundary layer thickness being lower than the diameter of the RDE [1,3].

Apart from determining the mass transfer coefficients, the RDE is also a useful tool when studying the electrochemical reaction kinetics, mainly due to the enhanced mass transport rate. In the case of an irreversible redox system, the kinetic parameters are usually determined by Tafel analysis from a charge-transfer limited region of a polarization curve [1]. From the linear dependence of the overvoltage on the logarithm of the current density, a slope and an intercept are evaluated according to the Tafel equation [1]. The charge-transfer coefficient α is then easily calculated from the slope. This value is useful for a determination of a reaction mechanism and/or the rate-determining step of the reaction. From the intercept of the extrapolated data with an x -axis, the exchange current density j_0 , which characterizes the rate of the electrochemical reaction in both an anodic and a cathodic direction at a reversible potential, can be determined. The reaction kinetics of an almost ideally reversible redox system, like e.g. $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, should preferably be evaluated using the Butler-Volmer equation. This is the result of two effects. First of all, the overall reaction rate in a rather wide potential range around the equilibrium potential is influenced by both a forward and a reverse electrode reaction. The experimentally available dependence of the current density logarithm on potential in the kinetically controlled region then, by definition, substantially deviates from simple linear dependence [1]. Secondly, the validity of the Tafel equation in the high current density region is limited by the mass transfer rate of the electroactive species to the electrode surface.

Though the RDE can be used in a variety of environments, the application of commercially available RDEs is generally limited to fairly ambient temperatures (below 80 °C) [8–10]. This limit is given mainly by the different thermal expansion coefficients of the electrode and the insulation material [11]. Above this temperature there is a danger of electrolyte leakage into the RDE, especially into the space between the disk and the insulating cylinder. This would have an unpredictable effect on the accuracy of the experiment. At the same time, it can lead to damage to the electrode. Examples of areas where the introduction of rotating electrode methodology would be of utmost importance are water electrolysis and fuel cells. Especially, a high temperature fuel cell with a proton-exchange membrane (HT PEM FC), operating in the temperature range of about 120–200 °C utilizes polybenzimidazole-type membranes doped with concentrated H_3PO_4 [12,13]. Therefore, in order for the testing of the catalyst electrode to be relevant, it has to be performed in an environment of concentrated H_3PO_4 and in the temperature range of HT PEM FC operation. However, current commercial RDEs do not permit such experiments to be performed, a fact which, to a large extent, complicates HT PEM FC catalyst testing in the corresponding environment. There are several examples of in-house made RDEs allowing operation at elevated temperatures in the literature, but the set-up is neither simple nor inexpensive [11,14]. Another type of hydrodynamic electrode which is suitable for a high-temperature environment is the rotating cylinder electrode (RCE) [15]. However, since the

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