



Research Paper

Building upon the Koutecky-Levich Equation for Evaluation of Next-Generation Oxygen Reduction Reaction Catalysts



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ARTICLE INFO

Article history:

Received 19 July 2017

Received in revised form 22 September 2017

Accepted 24 September 2017

Available online 28 September 2017

Keywords:

Koutecky-Levich equation

rotating disk electrode

oxygen reduction reaction

mass transport

reaction order

ABSTRACT

The performance of oxygen reduction reaction (ORR) catalysts has been substantially improved over the past several decades. These catalysts are evaluated for electrochemical activity in a rotating disk electrode (RDE) assembly using an oxygen saturated liquid electrolyte. Koutecky-Levich (K-L) analysis provides a simple and effective method to extract electrokinetic information by correcting for mass transport effects. We propose extensions to the K-L analysis to address some of the simplifying assumptions made during its derivation. In particular, we demonstrate that decreased concentrations of surface reactants contribute to measured overpotentials in a Nernst fashion, and can lead to an underestimation of catalytic activity. By applying a Nernst overpotential correction in conjunction with K-L analysis, more accurate measurements of the intrinsic reaction kinetics under mass transport limited conditions are possible. As the K-L method assumes a reaction order of unity, we also consider kinetic reaction order deviation from unity due to measurement conditions. We show that examining the dependence of the reaction order on overpotential can provide a straightforward technique to probe blocking effects of surface absorbents. We propose that these extensions to the K-L method can allow for increased versatility of the RDE technique for extracting electrokinetic parameters for ORR catalysts.

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1. Introduction

In the polymer electrolyte fuel cell (PEFC) community, extensive research and development efforts over the past few decades have led to the discovery of new surfaces and materials that catalyze the electrochemical oxygen reduction reaction (ORR) at rates much higher than those achieved previously [1–10]. Examples include polycrystalline surfaces, such as platinum-transition metal [11] or platinum-rare earth metal alloys [3,12–14], and single crystal surfaces, such as Pt₃Ni(111) [15]. Achievements in this regard have also been translated to high surface area catalysts, with nanostructured [16–19] materials having preferential faceting [20,21], or tailored alloyed/dealloyed systems [8–10,22–25], showing exemplary ORR activity. These surfaces and nanostructured catalysts are now routinely capable of achieving more than an order of magnitude activity enhancement over state of the art

carbon supported platinum (Pt/C), the commonly accepted benchmark catalyst.

In light of the need to evaluate catalysts and surfaces with greatly improved ORR activity, it is a worthwhile endeavor to revisit the techniques and methods used to extract electrokinetic information. This is a prudent approach due to the importance of conducting accurate evaluations of catalyst activity in all experiments ranging from fundamental electrochemical investigations to fuel cell testing. The conventional technique for evaluating electrokinetic activity for the ORR is the rotating disk electrode (RDE) technique. RDE experiments can involve a broad range of catalysts, including single crystal and polycrystalline materials, or high surface area catalysts that require drop casting an ink slurry onto an electronically conductive and chemically inert substrate (typically glassy carbon) to form a thin catalyst layer coated working electrode. The resulting working electrode is then rotated in a liquid electrolyte to induce the convective flow of reactant species (i.e., oxygen) toward the electrode surface. With the convective-diffusive flux of dissolved oxygen dictated by the electrode rotation rate, electrode potential-dependent current densities can be corrected for mass transport contributions. This

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Nomenclature

j_{tot}	total current density
j_{lim}	mass transport limited current density
j_k	kinetic current density
Λ	roughness factor, $\text{cm}^2_{\text{catalyst}}/\text{cm}^2_{\text{geometric}}$
$\eta_{measured}$	measured overpotential
η_k	kinetic overpotential
m	reaction order with respect to oxygen partial pressure
γ	kinetic reaction order
θ	portion of available active surface
C_R^*	concentration of surface reactant

allows for quantification of the kinetic current density (j_k), an intrinsic electrochemical reaction kinetic parameter. Values of j_k at a specific electrochemical potential are then reported as a figure of merit. In the past, the typically reported ORR activity has been at 0.9 V vs the reversible hydrogen electrode (RHE), but with significant improvements to catalytic activity achieved recently, values of 0.95 V vs RHE are now being reported in addition.

The Koutecky-Levich equation is a powerful and versatile tool that is commonly used for the correction of mass transport effects in RDE testing to obtain kinetic current densities. With its full derivation given in Ref. [26], the KL equation can be derived from two basic assumptions. The first is a linear diffusion model of reactants, whereby the surface reactant concentration C_R^* can be related to the reactant concentration in the bulk C_R^{Bulk} by the measured total current density j_{tot} and the mass transport limiting current density j_{lim} . This culminates in Eq. (1) shown below.

$$\frac{C_R^*}{C_R^{Bulk}} = \frac{j_{lim} - j_{tot}}{j_{tot}} \quad (1)$$

One important underlying assumption of this relationship is that the reactions corresponding to j_{lim} and j_{tot} are the same. For ORR, the reaction is generally referred to as reduction of oxygen to water. Nevertheless, there are possibly other processes that lead to reduction to hydrogen peroxide and even superoxide [27,28], which is gaining importance in alkaline solutions and non-noble metal catalysts [29–31]. For these cases, one shall use oxygen transport limiting rate and oxygen reduction rate to replace j_{lim} and j_{tot} , respectively.

The second assumption is that the electrochemical reaction follows first-order reaction kinetics. Assuming a first order reaction, the local current density j_{loc} is proportional to the multiplication of surface reactant concentration and the kinetic current density j_k (Eq. (2)), whereby j_k is a function of overpotential η , and is a product of reaction rate constant and reactant concentration C_R^0 under standard conditions (i.e., 298 K and 1 atm).

$$j_{loc} = j_k(\eta) \frac{C_R^*}{C_R^0} \quad (2)$$

If the surface roughness factor (as defined by Eq. (3)) Λ of the electrode is 1, one can combine Eqs. (1) and (2) as Eq. (4a) and obtain the reciprocal relationship as shown in Eq. (4b) as the Koutecky-Levich equation.

$$j_{tot} = \Lambda j_{loc} \quad (3)$$

$$\frac{j_{tot}}{j_k} = \frac{j_{lim} - j_{tot}}{j_{lim}} \quad (4a)$$

$$\frac{1}{j_{tot}} = \frac{1}{j_{lim}} + \frac{1}{j_k} \quad (4b)$$

In some cases, such as catalysts with ionomers and nanostructured catalysts, the linear diffusion assumption breaks down as oxygen supply is impeded by processes other than diffusion in the electrolyte. In such cases, it is practical to add another oxygen mass transport limiting current term [32] to Eq. (4b), thereby invalidating Eq. (1). The following discussion will set aside additional complexity arising from other diffusion processes, such as Pt/C powder catalysts with thick or nonuniform films and catalyst structures with strong interference from ionomers so that analytical approaches such as the K-L method are still meaningful.

The kinetic current density j_k is a function of overpotential η . Assuming a single rate limiting step for the multi-electron process of oxygen reduction, j_k can be formulated with a Butler-Volmer type of relationship as shown by Eq. (5), where j_0 is the exchange current density, α is the transfer coefficient, the product of symmetry factor and the number of electrons, n_{RLS} , transferred in such a elementary step, F is the Faraday constant, and R is the ideal gas constant. For modeling reaction kinetics of Pt catalysts, the value of α is taken as unity based on a Tafel slope of 59 mV/dec. The value of n_{RLS} in Eq. (5) is set to be 1, as the rate limiting steps for ORR on Pt are single electron/proton transfer steps either to adsorbed oxygen or adsorbed hydroxyl species [33–35].

$$j_k(\eta) = j_0 \left\{ \exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left[-\frac{(\alpha - n_{RLS}) F \eta}{RT}\right] \right\} \quad (5)$$

In the first part of this work, we will discuss how the development of increasingly active catalysts can lead to an overestimation of kinetic overpotential during RDE measurements. The effect of lowered surface reactant concentration on the kinetics has been considered by the KL method. Nevertheless, according to the Nernst equation, the measured overpotential, $\eta_{measured}$, also contains a contribution associated with the lowered surface reactant concentration. When compared at the same absolute electrochemical potential (i.e., 0.9 V vs RHE), more active catalysts will ultimately result in lower surface reactant concentrations and thus larger contribution to the Nernst losses. In other words, higher performance catalysts are compared at a lower kinetic overpotential η_k , potentially leading to an underestimation of intrinsic catalytic activity (i.e., overestimation of η_k).

$$\eta_k = \eta_{measured} + \frac{RT}{nF} \ln \frac{C_R^*}{C_R^{Bulk}} \quad (6)$$

The second part of this paper discusses the reaction order of the ORR, which is a key underlying assumption of the reciprocal relationship of the K-L method. Theoretical reaction orders will be derived and compared with experimental values obtained using polycrystalline platinum electrodes as an example. The deviation of reaction order from unity can provide detailed information on surface blocking effects and offer justification for appropriate measurement protocols.

2. Experimental

A 0.196 cm^2 polycrystalline platinum disk was used for the example of electrochemical measurements on the flat substrate. The polycrystalline platinum disk was first mechanically polished with 0.05 μm alumina slurry to obtain a flat, mirror-like finish, and then annealed with a butane flame. The disk was assembled in a RDE tip for activity evaluation. The electrolyte was diluted from 70% perchloric acid (Veritas Doubly Distilled, GFS chemicals) to 0.1 mol/L with ultrapure water (18.2 M Ω cm, TOC <5 ppb). A three-

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