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Review Article

Hidden in plain sight: unlocking the full potential of cyclic voltammetry with the thin-film rotating (ring) disk electrode studies for the investigation of oxygen reduction reaction electrocatalysts

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Abstract

Cyclic voltammetry conducted with a thin-film rotating disk electrode, or ring-disk electrode (CV-TF-R(R)DE) is a very popular *ex situ* tool for the rapid screening of electrocatalysts for their activity in oxygen reduction reaction. Despite its popularity and broad use, in most instances only a small part of the information that could be accessed by CV-TF-R(R)DE is actually used by scientists in their research. This work outlines both innovative and more traditional (but half-forgotten) ways of using CV-TF-R(R)DE to its optimal or full potential in the ongoing quest to study the most relevant features of oxygen reduction reaction electrocatalysts and quickly identify the most promising candidates for their applications in fuel cells or other electrochemical devices.

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Keywords

Oxygen reduction reaction (ORR), Mechanism, Cyclic voltammetry (CV), Rotating disc electrode (RDE), Rotating ring-disk electrode (RRDE).

Introduction

The oxygen reduction reaction (ORR) is a key process for electrochemical energy conversion and storage devices such as fuel cells (FCs) and metal-air batteries [1–3]. In particular, the ORR bottlenecks the operation of low-temperature FCs such as proton-exchange membrane FCs and anion-exchange membrane FCs because of the substantial overvoltage associated with it [4–6]. Suitable ORR electrocatalysts (ECs) are needed to ensure that the performance level of the devices complies with the requirements set by the applications [7]. The development of high-performing, durable and inexpensive ORR ECs is a major goal of applied electrochemistry research, that is currently exploring several widely different approaches, such as: Pt-alloy ECs, ECs possibly exhibiting exotic morphologies [8,9]; development of platinum group metal-free ECs [10–13], among many others [14]. Even though it would be best to test each new developmental ORR ECs in a full-cell membrane electrode assembly as close as possible to a prototype device, the associated substantial investment in terms of time and efforts makes this approach not feasible [15,16]. To address this issue and quickly screen several types of very different ORR ECs at early developmental stages, *ex situ* approaches are commonly adopted [17]. The most popular of such approaches is cyclic voltammetry with a thin-film rotating disk (or ring-disk) electrode, abbreviated here as CV-TF-R(R)DE [18–21].

CV-TF-R(R)DE for the determination of the catalysts' intrinsic kinetic performance

CV-TF-R(R)DE is widely used in the literature to determine the intrinsic ORR kinetic performance of an EC [19,22–24]. In the *conventional* approach commonly adopted for data analysis, the first step covers the correction of iR drops from the measured currents [25]. Subsequently, the ORR faradic current (i_{ORR}) is determined by subtracting the capacitive current i_{cap} from the total iR -corrected current i_{tot} (refer Eq. (1)) [21,26]:

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$$i_{ORR} = i_{tot} - i_{cap} \quad [1]$$

i_{cap} is typically measured collecting CV profiles on the same electrode where i_{tot} is determined, but under an inert atmosphere. In a second step, the contributions arising from the mass transport of oxygen from the bulk electrolyte to the active sites are removed as follows (refer Eq. (2)) [19,27]:

$$\frac{1}{i_{ORR}} = \frac{1}{i_{k,ORR}} + \frac{1}{i_d} \rightarrow i_{k,ORR} = \frac{i_{ORR} \cdot i_d}{i_d - i_{ORR}} \quad [2]$$

where $i_{k,ORR}$ is the kinetic current in the ORR and i_d is the diffusion-limited current as determined on the current plateau at low electrode potentials. It is pointed out that Eq. (2) is valid only on the assumption that the partial order γ of the ORR on the EC/electrolyte interface in respect to the concentration of the oxygen reactant is equal to 1. This was verified by experiments on conventional Pt/C ECs [28]; accordingly, Eq. (2) is almost universally adopted in the literature [19]. However, in principle γ might be different from 1, and this could be revealed by distortions in the mixed kinetic/diffusion-controlled region close to the diffusion-limited plateau [29]. In this case, to obtain $i_{k,ORR}$ from i_{ORR} and i_d it is necessary to determine experimentally γ as described elsewhere [28] and subsequently remove the contributions arising from the mass transport of oxygen by means of the following Eq. (3) [30].

$$i_{k,ORR} = \frac{i_{ORR}}{\left(1 - \frac{i_{ORR}}{i_d}\right)^\gamma} \quad [3]$$

In the case of conventional platinum-based ECs, the plateau is detected at $E < 0.6$ V vs. RHE. The performance of an ORR EC is then gauged by evaluating $i_{k,ORR}$ at a certain potential (typically, 0.9 V vs. RHE) against a benchmark [21,23]. Very often, $i_{k,ORR(0.9V)}$ is normalized on other properties of the EC such as: (i) the mass of precious metals on the electrode tip (mass activity, $i_{m,ORR(0.9V)}$); and/or (ii) the surface area of the active sites found on the electrode tip (surface activity, $i_{s,ORR(0.9V)}$) [21–23]. The latter is typically evaluated by other independent approaches such as the integration of the charge associated with the stripping of a probe specie (e.g., CO, H₂, NO₂) [31–33] that adsorbs selectively on the active sites of the EC.

This 'conventional' approach suffers from shortcomings that arise from the steps involved in the removal of the various spurious contributions of i_{tot} in the evaluation of $i_{k,ORR}$. The removal of the capacitive currents may yield distorted results as $i_{ORR} < 0.1 \cdot i_{cap}$. Indeed, i_{cap} of the electrode may change slightly depending on the gas the electrode tip is exposed to. Typically, i_{cap,O_2} is slightly larger than $i_{cap,inert\ gas}$ because O₂ facilitates the formation of charged oxygenated species on the surface of the electrode tip, that raise its capacitance. Another issue is that in

Eq. (2) and Eq. (3), the precise value of i_d only slightly affects $i_{k,ORR}$ but only on the condition that the overall correction is 'small' (i.e., $i_{k,ORR} < 1.5 i_{ORR}$). On the other hand, because $i_{k,ORR}$ increases dramatically as the η_{ORR} is raised, very small errors in the determination of i_d may affect significantly $i_{k,ORR}$, jeopardizing the accuracy of the obtained figures at large ORR overpotentials. The aforementioned shortcomings become highly relevant when, at the potential of interest (typically, 0.9 V vs. RHE) $i_{k,ORR}$ is either: (i) very small ($i_{k,ORR} \sim i_{ORR} < 0.1 i_{cap}$); or (ii) much larger than i_{ORR} ($i_{k,ORR} > 1.5 i_{ORR}$). In the first case (typical of 'Pt-free' ORR ECs operating in an acid environment and exhibiting large capacitive currents due to a large specific surface area), the values of $i_{k,ORR(0.9V)}$ are too small to be meaningful [34]. In the second case (typical of high-performing ORR ECs exhibiting exotic Pt morphologies), the values of $i_{k,ORR(0.9V)}$ become stellar but quite meaningless [35].

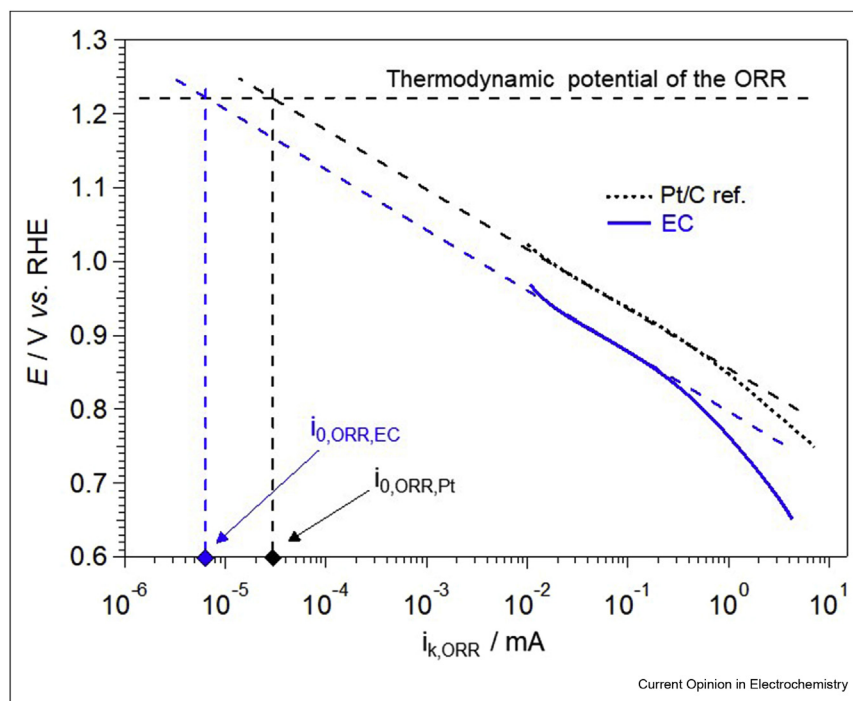
One way to address the shortcomings of the conventional approach to analyse kinetic ORR data is to take into consideration only $i_{k,ORR}$ values, where the corrections due to capacitive and mass-transport phenomena are small. These data are plotted in the semilogarithmic scale (Tafel plots) and extrapolated to the thermodynamic potential of the ORR, thus allowing to gauge the exchange current of the EC in the ORR ($i_{0,ORR,EC}$) [36,37]. Figure 1 displays how $i_{0,ORR}$ is determined both for an EC and for a conventional ORR benchmark (i.e., Pt/C ref.).

Figure 1 assumes that all the ECs exhibit the same Tafel slope (ca. 70 mV·dec⁻¹). This assumption is validated from experimental data displayed in the literature and considering that, for most ORR ECs (both based on platinum group metal-free and 'Pt-free'), at the lowest η_{ORR} the kinetics are bottlenecked by the same process (i.e., the first electron transfer from a surface blocked by oxygen adsorbates to the incoming O₂ molecule) [38–40]. With respect to the 'conventional' approach, the advantage of the proposed analysis approach that takes into consideration $i_{0,ORR,EC}$ is that it is possible to compare simultaneously, and at the same level of accuracy that is ensured by the small corrections to account for nonfaradic processes, the performance of several different ECs that exhibit widely disparate values of η_{ORR} . Since $i_{0,ORR,EC}$ can easily vary over several orders of magnitude, a more handy figure of merit to gauge the intrinsic ORR kinetics of an EC in comparison with that exhibited by an ORR benchmark Pt/C ref. is the following (refer Eq. (4)) [41]:

$$I = \log_{10} \left(\frac{i_{0,ORR,EC}}{i_{0,ORR,Pt}} \right) \quad [4]$$

In summary, I allows for the comparison in the same 'ideal' conditions (i.e., at the thermodynamic ORR

Figure 1



Determination of the exchange current for both an EC and an ORR benchmark Pt/C ref. EC, electrocatalysts.

potential) of the kinetic features of the electrochemical interface between ECs, electrolyte, reactants, and products in widely different ECs, irrespectively of all other additional parallel phenomena that could take place in practice as the ORR overpotential is reduced (*e.g.*, side reactions, formation of passivating oxide layers).

CV-TF-R(R)DE to gauge the morphology/transport features of ORR ECs

At large η_{ORR} ($E < 0.6$ V *vs.* RHE for typical Pt-based ECs) the oxygen reduction currents registered in CV-TF-R(R)DE measurements are bottlenecked by the transport of O_2 from the bulk electrolyte to the active sites of the EC deposited on the R(R)DE disk [19,42]. A diffusion-limited plateau is formed at the current i_d . In conventional CV-TF-R(R)DE measurements, the values of i_d can be determined by means of the Levich equation (refer Eq. (5)) [27]:

$$i_d = 0.62n_{\text{ORR,EC}}FAD^{2/3}\nu^{-1/6}C_0\omega^2 = b_{\text{EC}}\omega^2 \quad [5]$$

where: n_{ORR} is the overall number of electrons exchanged during the ORR by the EC; F is the Faraday constant; A is the geometric area of the disk electrode; D and C_0 are, respectively, the diffusion coefficient and the bulk concentration of O_2 in the support electrolyte; ν is the kinematic viscosity of the support electrolyte; and ω is the

rotation rate of the R(R)DE tip [27]. It is pointed out that Eq. (5) can be applied indy check the de toin ideal CV-TF-R(R)DE experiments after assumptions are expected to be true: (i) the layer containing the EC under scrutiny covers uniformly the disk on the R(R)DE tip; (ii) the area of the active sites in the EC layer is comparable or larger than that of the disk; (iii) the thickness of the EC layer is much lower than the oxygen-depletion layer facing the disk of the R(R)DE tip; and (iv) the R(R)DE tip is spun quickly enough to allow for the formation of a laminar oxygen-depletion layer [19,27]. Under these assumptions, the amount of information that can be extracted using the Levich equation is quite limited. In the literature, the conventional approach for data analysis consists the following steps: (i) a certain potential is selected on the diffusion-limited plateau on the CV-TF-R(R)DE trace; (ii) ω^2 is varied, and the corresponding i_d values at the selected potential are determined; and (iii) the resulting datapoints are fitted with a line, whose slope b_{EC} is compared with that obtained on a R(R)DE covered by a Pt/C benchmark, indicated as b_{Pt} [43]. In Eq. (5), if both the EC under scrutiny and the Pt/C benchmark are measured on the same R(R)DE tip and in the same conditions in terms of temperature, chemical composition of the support electrolyte and partial pressure of O_2 in the system, the only variable term is $n_{\text{ORR,EC}}$, *i.e.*, the number of electrons exchanged during the ORR at the potential selected to determine i_d . Since in first approximation at $E < 0.6$ V *vs.* RHE the $n_{\text{ORR,Pt}}$ of a Pt/C benchmark is 4 [44,45], the following holds true (refer Eq. (6)):

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$$n_{ORR,EC} = n_{ORR,Pt} \cdot \frac{b_{EC}}{b_{Pt}} = 4 \cdot \frac{b_{EC}}{b_{Pt}} \quad [6]$$

In summary, the entire Levich analysis is typically carried out exclusively to measure $n_{ORR,EC}$ of an EC at the potential selected to read i_d . In recent times, $n_{ORR,EC}$ is most often determined directly and much more quickly through CV-TF-RRDE measurements [46,47]. Hence, the Levich analysis has somewhat fallen out of common use. This is unfortunate, as the potential of the Levich approach for the study of ORR ECs could be significant.

It is pointed out that in several instances, and in particular when CV-TF-R(R)DE studies are carried out on Pt-free ECs, the thickness of the EC layer on the R(R)DE disk becomes comparable with that of the oxygen-depletion layer facing the disk of the R(R)DE tip (*ca.* 10 microns at $\omega < 3600$ rpm) [48]. It was also shown that, in some instances, the b_{EC} of a nominally thin EC layer ($d \approx 2$ microns) can be larger than b_{Pt} detected in the same experimental conditions [41]. Both these results can be interpreted relaxing some of the assumptions on the basis of the Levich equation, as follows: (i) D becomes a function of the morphology and mass transport features of the EC layer, is relabelled $D_{EC}(M)$ and accounts for the transport of O_2 through both the oxygen-depletion layer facing the disk of the R(R)DE tip and the EC layer itself; this latter could either inhibit or promote O_2 transport; (ii) A is relabelled $A_{EC}(M)$ and is no longer the geometric area of the R(R)DE disk, but becomes a function of the morphology of the EC layer. A is typically lower than $A_{EC}(M)$ as the latter can also account for the roughness of the EC layer. It is highlighted that the literature already reports instances where the ORR currents of R(R)DE set ups are much higher than those predicted on the basis of the Levich theory [49,50]. However, these results are obtained with highly porous electrode layers, whose thickness is much larger than the 1–10 microns assumed here [51,52]. On the basis of these considerations, it is possible to define the following figure of merit, B' , that allows us to use CV-TF-R(R)DE measurements to achieve a first, qualitative estimate of the transport features of EC layers including the EC under scrutiny (refer Eq. (7)):

$$B = \frac{b_{EC}}{b_{Pt}} = \frac{0.62 n_{ORR,EC} F A_{EC}(M) D_{EC}(M)^{2/3} \nu^{-1/6} C_0}{0.62 n_{ORR,Pt} F A_{Pt}(M) D_{Pt}(M)^{2/3} \nu^{-1/6} C_0} \\ = \frac{n_{ORR,EC} A_{EC}(M) D_{EC}(M)^{2/3}}{n_{ORR,Pt} A_{Pt}(M) D_{Pt}(M)^{2/3}} \quad [7]$$

It is pointed out that in principle the ratio $n_{ORR,EC}/n_{ORR,Pt}$ can be determined directly by CV-TF-RRDE

measurements, thus allowing to isolate the contributions due to $A_x(M)$ and $D_x(M)$ ($x = EC, Pt$) in the figure of merit B' , as follows (refer Eq. (8)):

$$B' = B \frac{n_{ORR,Pt}}{n_{ORR}} = \frac{A_{EC}(M) D_{EC}(M)^{2/3}}{A_{Pt}(M) D_{Pt}(M)^{2/3}} \quad [8]$$

If $B' > 1$, the morphology/transport properties of the EC layers including the EC under scrutiny are improved in comparison with those of a Pt/C benchmark. However, it is possible to obtain important qualitative information directly from B (refer Eq. (7)) only on the basis of simple physicochemical considerations even without having to determine explicitly B' by measuring the $n_{ORR,EC}/n_{ORR,Pt}$ ratio through CV-TF-RRDE experiments.

It is well known that at $E < 0.6$ V vs. RHE, on the diffusion-limited plateau of the CV-TF-R(R)DE traces, $n_{ORR,Pt} \approx 4$ [26,44,45,53]; even in the cases when the selectivity of a given EC should be improved in comparison with a Pt/C benchmark, such an improvement would be very small in absolute terms. Consequently, the following relation holds true (refer Eq. (9)):

$$\text{Slightly more than } 1 > n_{ORR,EC}/n_{ORR,Pt} > 0.5 \quad [9]$$

$n_{ORR,EC}/n_{ORR,Pt} = 0.5$ for an ORR ECs only able to reduce O_2 to H_2O_2 by exchanging 2 electrons [44]. By considering Eq. (7) and Eq. (9) together, it is clear that B can be lower than 1 owing both to a low number of electrons exchanged during the ORR, or to a poor morphology/porosity of the EC layer, inhibiting O_2 transport. However, $B > 1$ can only be obtained if the transport features of the EC layers including the EC under scrutiny are improved in comparison with those of a Pt/C benchmark, more specifically, when the morphology of the EC allows for a better use of the concentration of the metal sites.

Conclusions and outlook

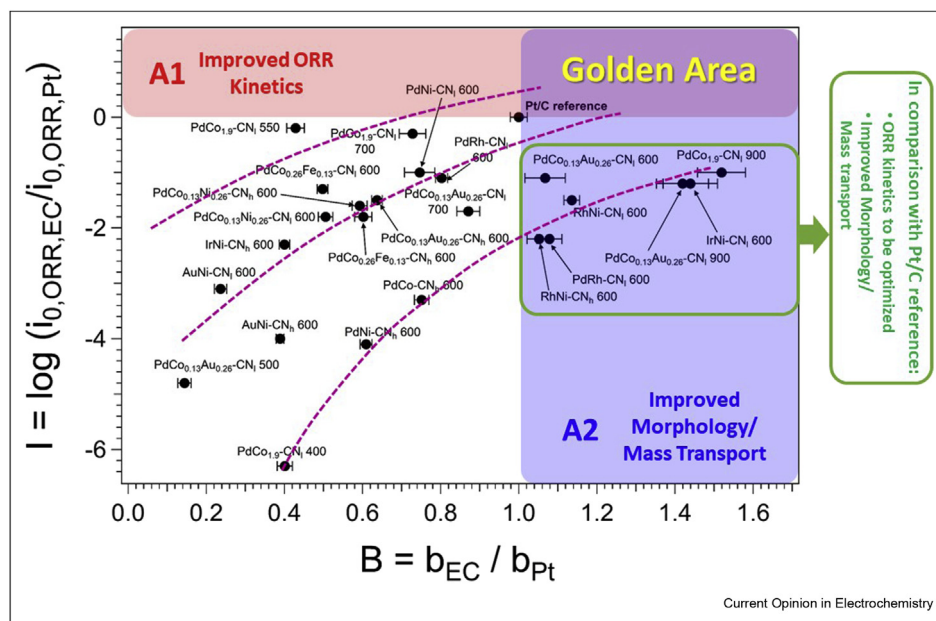
In this work, it is shown that CV-TF-R(R)DE studies can be used for the following two purposes:

- To study in detail the ORR kinetic features of vastly different ECs. The determination of $i_{0,ORR,EC}$ allows us to carry out quantitative performance comparisons at the same high level of accuracy for all the ECs, without risking serious distortions due to the excessive impact of corrections during data analysis. A

simple figure of merit $I = \log_{10} \left(\frac{i_{0,ORR,EC}}{i_{0,ORR,Pt}} \right)$ is defined,

that allows us to gauge in a very straightforward way how well a given EC is able to carry out the ORR. If $I > 0$, the EC performs better than a Pt/C reference.

Figure 2



I vs. B morphokinetic (MK) correlation map. CV-TF-RDE measurements are carried out at the following experimental conditions: loading of 'active metal' on the electrode: $15 \mu\text{g cm}^{-2}$; $\text{P}_{\text{O}_2} = 1 \text{ atm}$; $\omega = 1600 \text{ rpm}$; scan speed 5 mV s^{-1} . The dashed lines are meant as a guide for the eye.

- To achieve a quantitative understanding whether a given EC exhibits improved morphology/mass transport features in comparison with a Pt/C benchmark. A simple figure of merit is defined, $B = \frac{b_{\text{EC}}}{b_{\text{Pt}}}$, starting from the slopes of Koutecky–Levich plots b_x ($x = \text{EC}, \text{Pt}$) and without the need of a RRDE set up. When $B > 1$, the morphology/mass transport features of a given EC are improved in comparison with the Pt/C reference.

It can then be proposed an I vs. B morphokinetic (MK) correlation map where to report the CV-TF-R(R)DE results of even widely different ECs. The position of the results on such map allows for the clear identification of which ECs are the most promising in comparison with a Pt/C benchmark considering both ORR kinetics and morphology/mass transport. For the sake of illustration, we consider a broad family of ORR ECs exhibiting the following features: (i) one 'active metal' providing the most of the performance: either Pt, Ir, Rh, or Au; (ii) one or more 'cocatalyst' boosting the ORR performance of the 'active metal': Fe, Co, Ni, Au; (iii) a carbon nitride matrix (CN_x) supporting the active sites and comprising a concentration of N either lower than 5% ($x = l$) or higher than 5% ($x = h$); and (iv) a pyrolysis temperature T_f ranging between 400 and 900 °C [41,54]. Measurements were carried out with a CV-TF-RDE set up. The location of CV-TF-RDE results for the ORR performance of these ECs is displayed in Figure 2.

In the MK map shown in Figure 2, it is possible to identify both: (i) an area A1 where the ORR kinetics of an EC is better than the Pt/C benchmark; and (ii) an area A2 where the morphology/mass transport features of an EC are better than the Pt/C benchmark. A1 and A2 overlap in a 'golden area'. If an EC should fall here, it would exhibit improved kinetics and morphology/mass transport features in comparison with the Pt/C benchmark and would be highly promising for implementation in a single proton-exchange membrane FCs to test its features in more realistic conditions. For the specific ECs displayed in Figure 2, some exhibit improved morphology/mass transport features than the Pt/C benchmark (e.g., PdCo_{1.9}-CN₁ 900), although their pure kinetics still needs to be optimized.

In conclusion, a careful design of CV-TF-R(R)DE experiments and a suitable data analysis allows us to compare at the same level of accuracy even widely different EC taking into consideration both kinetic and morphology/mass transport features. This allows us to: (i) expand significantly the scope of the CV-TF-R(R)DE studies in comparison with the state of the art; and (ii) better identify promising ORR ECs for application in low-temperature FCs by using a simple MK correlation map.

Declaration of competing interest

Nothing declared.

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