



# Electrochemistry needs electrochemists: “goodbye to rotating discs”

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## Abstract

The essential need for expert, fully trained electrochemists in the successful application of the subject is illustrated with several examples including the use of rotating electrodes and impedance spectroscopy where the use of the techniques in “black box” mode non-experts is likely to lead to disappointment or embarrassment.

Years ago, the Compton Group developed a chemical sensor for a toxic gas in collaboration with a large, international company. The work started as a speculative academic research project developing a mediated, pH-sensitive electrochemical approach, and then on the basis of some promising results moved to the company for adaptation into a benchtop sensor. This transpired to be extremely successful so it was judged worth testing in the real world. At this point the project transferred to a different part of the company for “engineering” and was put in the hands of the appropriate experts. The resulting prototype sensor was then sent for field testing at a rather large cost. The results from the field were unambiguous—the sensor just did not work. No response was obtained even when naturally exposed to large amounts of the target gas. Given the expenditure in getting to that point, a serious inquest was held into what went wrong. At this point, it was discovered that the expert engineers had decided that the chemical recipe for the electrolyte provided to them was inconvenient to implement so had swapped the recommended sulfuric acid electrolyte for water! Much less corrosive and far easier to handle! Needless to say, on restoring the acid so as to fix the pH, the sensor worked perfectly, from which we conclude—chemistry matters!

At present, the development of new batteries and fuel cells, indeed energy technology most generally, is mostly in the hands of engineers and materials scientists. This, in

the light of the above experience, may be ill advised! To highlight the potential pitfalls of excluding electrochemists we will, as the first example, consider the use of the rotating disc (RDE) and the rotating ring disc electrode (RRDE) for the study of electrocatalysis in general and the oxygen reduction reaction (ORR) in particular, the latter being a key reaction for some energy technologies.

Rotating disc electrodes are attractive since they allow steady-state voltammetry to be performed at a (disc-shaped) macroelectrode so that the current–voltage characteristics can be examined under both electrode kinetic and transport control, as the convective-diffusion to the electrode has been rigorously characterized by Levich [1]. The RRDE was invented by Frumkin and Nekrasov and first reported in 1959 [2, 3] with Bruckenstein (USA) and Albery [4–6] (Great Britain) the soonest to imitate outside of the USSR. Frumkin is, of course, widely regarded as the “Father of Modern Electrochemistry” [7–9] with profound contributions across the breadth of the subject.

In essence, the RRDE is a rotating disc electrode surrounded by a coaxial ring electrode with the two electrodes separated by an insulating gasket allowing the potential of the two electrodes to be controlled independently of each other via a bi-potentiostat. In this way, steady-state voltammograms can be recorded on the ring electrode as a function of the potential of the disc electrode and reflect chemical species formed at the disc that are being swept by the rotation-induced convective flow to the ring surface where they may undergo electrolysis revealing their voltammetric fingerprint so allowing identification. Thus, the purpose of the device as explained by its pioneers [2] is the study of unstable intermediates formed during the electrode reaction on the disc electrode. Under favorable conditions, the lifetimes of the intermediates can be estimated. The latter

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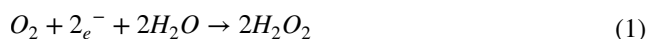
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usually requires numerical simulation [3, 10–12] except for ideal simple cases where analytical approximations were derived first by Ivanov and Levich [13] which were later developed further by Bruckenstein [14] and then Albery [5]. Interestingly, many contemporary American and Western European electrochemists will tell you that the “RRDE was invented by Albery and Bruckenstein.” It was not. Moreover, the theoretical basis of the transport at a RRDE due to Ivanov and Levich [13] also predates their theoretical work by ca six years. Relative neglect of the inventive prior art persists; see for example [15] where authors appear unaware that the “approximate” theory of Ivanov and Levich was *quantitatively* consistent with the experiments of Nekrasov and Frumkin [2], as next described.

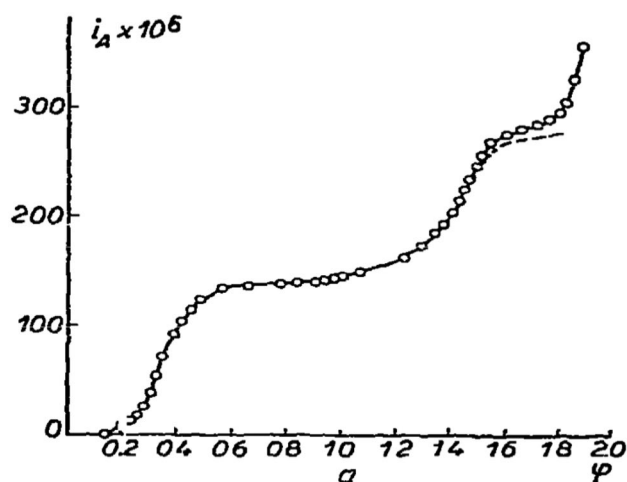
Frumkin and Nekrasov presented two illustrations of the RRDE technique. They first studied the two electron reduction of p-benzoquinone in 1 M aqueous solution to form the hydroquinone using a RRDE with both electrodes made of platinum and reportedly capable of rotating at 15,000 rpm. They showed that the ring “collected” 38% of the hydroquinone generated on the disc electrode for the particular electrode sizes used and by comparison with theory confirmed that the product was both kinetically stable, at least in the voltammetric timescale accessed and that hydroquinone was the exclusive product of the disc electrode reaction. Of course, the same information could have been obtained by conducting cyclic voltammetry at the disc electrode without the need for rotation. However, the ability to measure currents under steady-state conditions was, *at the time*, thought to be experimentally preferable. That said, it is interesting to note that Frumkin and Nekrasov carefully report their experimental “collection efficiency” data to two significant figures. Albery and Bruckenstein [5, 16] confidently assert three significant figures with error estimates ranging from 0.2 to 0.5% but do not discuss the current measurements, their accuracy, or if any baseline corrections were applied. Curiously, they do not include as co-authors of the paper the two scientists they acknowledge as having carried out the extensive experiments!

In the second RRDE study, the disc was made of amalgamated gold, the ring of gold, and the reaction studied was the reduction of oxygen in aqueous base which was seen to proceed in two stages:



as revealed by the observation of two voltammetric waves at the disc electrode (see Fig. 1).

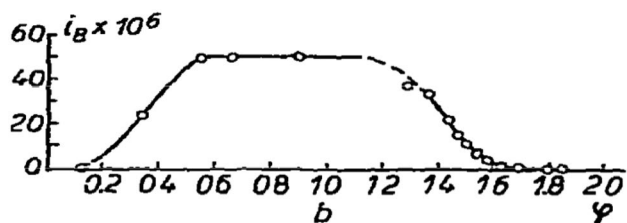
The ring current measured at a potential corresponding to the oxidation of hydrogen peroxide is shown as a function of the disc potential in Fig. 2. It is evident that in the



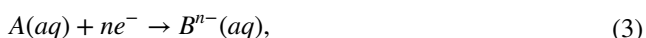
**Fig. 1** Polarization curve measured for oxygen reduction reaction conducted in 0.1 M NaOH. Potential is given in V vs normal calomel electrode and current in A. The original curve was published in 1959 work by Frumkin and Nekrasov [3]

region of the first wave on the disc that hydrogen peroxide is the stable product of the disc electrode reaction but that in the region of the second wave it is an intermediate product with no hydrogen peroxide formation at disc potentials corresponding to the limiting current of the second wave. The latter was therefore inferred to lead exclusively to the formation of water (or hydroxide) and it was possible to infer and electrochemical rate law and rate constant for the reduction of hydrogen peroxide on the disc electrode since the ring signal, convoluted by the theoretical collection efficiency, gave an indication of the amount of hydrogen peroxide at the disc surface.

Both the RDE and the RRDE have been used taken up by the “energy community” for the study of electrocatalytic materials. In the former case, it has been typical to use the so-called Koutecky-Levich (KL) approach for the analysis of steady-state voltammetric data at variable rotation speeds [17, 18] to find heterogeneous rate constants for electrode reactions which are controlled by both diffusion and kinetics. Assuming a process of the form.



**Fig. 2** The ring current measured in A at a potential corresponding to the oxidation of hydrogen peroxide is shown as a function of disc potential. Potential is given in V vs normal calomel electrode. The original curve was published in 1959 work by Frumkin and Nekrasov [3]



the total flux,  $j$ , at the disc electrode is given by

$$\frac{1}{j} = \frac{1}{kc_\infty} + \frac{1}{\frac{Dc_\infty}{\chi}} \quad (4)$$

[19], where  $k$  is the potential dependent rate constant of the reaction,  $c_\infty$  is the bulk concentration of the reacting species in the electrolyte,  $D$  is the diffusion coefficient, and  $\chi_D$  is the thickness of the diffusion layer given by:

$$\chi_D = 1.61\omega^{-\frac{1}{2}}\nu^{\frac{1}{6}}D^{\frac{1}{3}} \quad (5)$$

where  $\omega$  is the speed of the rotation of the electrode,  $\nu$  is the kinematic viscosity, and  $D$  is the diffusion coefficient of the species.

Thus, a plot of reciprocal flux (or current) against the reciprocal of  $\sqrt{\omega}$  gives a straight line with an intercept which allows the inference of  $k$  (and its potential dependence). This approach is well illustrated by the elegant investigation of the kinetics of the Fe(II)/Fe(III) system by Vielstich and Jahn [20] at a platinum rotating disc electrode.

From the above, it seems that the KL rotating disc approach is an excellent method for determining electrochemical rate constants and hence inferring whether any particular electrode surface is electrocatalytic or not in comparison with others. However, electrochemists immediately recognize the need for caution. First, almost pedantically, Eq. (5) is an approximation which works only for species having a relatively low diffusion coefficient in comparison with the kinematic viscosity ( $\nu$ ) of water which has a value of  $0.01 \text{ cm}^2 \text{ s}^{-1}$  near 298 K leading to a high Schmidt number ( $Sc = \nu/D$ ). More fully, the diffusion layer thickness is given by [21]:

$$\delta_D = 1.61 \left(\frac{D}{\nu}\right)^{\frac{1}{3}} \left(\frac{\nu}{2\pi\omega}\right) 1/2 [1 + 0.298 \left(\frac{D}{\nu}\right)^{\frac{1}{3}} + 0.14514 \left(\frac{D}{\nu}\right)^{\frac{2}{3}}] \quad (6)$$

Thus, for example when studying protons,  $\text{H}^+$ , for which the diffusion coefficient at a similar temperature is, in comparison with many other solution phase species, anomalously high (ca  $9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [22, 23]) as a result of the Grotthuss hopping mechanism [24], the use of the extended expression for the diffusion layer is necessary for accurate work. The comparable diffusion coefficient of oxygen is  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [25] putting this analyte also on the cusp of necessity.

Second and very much more importantly, Johnson and colleagues [26] have pointed out that Eq. (1) is very often an approximation for multi-electron processes, since they typically involve a sequence of electron transfer events (E) and chemical steps (C) which can render the simple KL analysis invalid. The paper by Johnson and team [26] is essential preparation for anyone contemplating using the KL approach.

In addition to identifying numerous mechanistic cases where the (electrochemical) complexity precludes the possibility of a linear KL plot, they also emphasize the essential need to make measurements over wide range of rotation speeds, suggesting a range of 50–10,000  $\text{rev min}^{-1}$ , mirroring the equipment capabilities of Frumkin and Nekrasov [2] but not all more recent studies and, of course, placing significant demands on the cell volumes studied experimentally if the assumption of the RDE immersed in an infinite medium is to be approximated.

A third caveat arises since the KL theory applies for processes at *flat* rotating disc electrodes. In current popular practice, electrodes are often modified with nanoparticles or micro-particles to facilitate electrocatalysis, or else disc-shaped composites are studied. Thus, depending on the approach to fabrication and the extent of coverage, the surface may be partly active or, in the case of composites, have significant roughness and/or porosity. In all cases, the surfaces of the modified electrode or composite are unlikely to be flat in contrast to, for example, the RDEs used successfully by Vielstich and Jahn [20]. At one limit of roughness where the diffusion layer is larger than the scale of the surface roughness, it is important to note that the transport limited current reflects the geometric area of the electrode and not the true electrochemical area. At the other extreme, Table 1 shows illustrative examples of nanoparticle-modified electrodes studied as electrocatalysts for the ORR. Note that these are just a few chosen from the myriad of reports of ORR catalysts in the literature.

The effects of electrode roughness and/or porosity on KL analysis have been studied via simulation [35] leading to the recognition of the importance of the ratio,  $\psi$ , where

$$\psi = A_{act}/A_{geo}, \quad (7)$$

in which  $A_{act}$  is the surface area of the electroactive particles and  $A_{geo}$  is the geometric area of the electrode. Quantitative theory was developed under the assumption that the surface roughness is smaller than the diffusion layer thickness, and that the particles are conductive so that electrolysis is confined to at or near the electrode surface, and led to the qualitative conclusions that when  $\psi \neq 1$  either as a result of either partial coverage or porosity effects then the rate constants from KL analysis are apparent not real rate constants with the apparent rate constants typically being a function of  $\psi$ . In particular for values of  $\psi > 1$ , the apparent rate constant will be larger than the true rate constant whereas the converse is the case for  $\psi < 1$ . Thus, purely because of the available surface area of active material, positive and negative catalytic effects can be inferred. Simply by increasing the active surface area, for example by shrinking the size of the modifying particles when studying a fixed mass of the particles, can lead to an increase in the apparent rate constant

**Table 1** Examples of nanoparticle-modified electrodes studied as electrocatalysts for the ORR using RDE

Author	Year	Title
Zoski et al. [27]	2011	Intrinsic ORR activity of Pt nanoparticles
Jirkovsky et al. [28]	2010	Dependency of rate constant and OR activity on Au nanoparticle size Kinetics of electrocatalytic reduction of oxygen and hydrogen peroxide on dispersed gold nanoparticles
Jaouen et al. [29]	2010	Non-precious metal catalysts for oxygen
Guo et al. [30]	2012	PtFe nanoparticles on graphene for ORR
Liu et al.	2012	Bimetallic Pd–Pt nanoparticles for ORR
Si et al. [31]	2013	Pt nanodendrites with enhanced ORR activity
Wang et al. [32]	2020	Single-phase Ru <sub>1-x-y</sub> MnxCo <sub>y</sub> O <sub>2</sub> nanoparticles as highly effective oxygen reduction electrocatalysts in alkaline media with enhanced stability and fuel-tolerance
Lusi et al. [33]	2021	Oxygen reduction reaction on Pd nanoparticles supported on novel mesoporous carbon materials
Nandan et al. [34]	2021	Atomic Arrangement Modulation in CoFe Nanoparticles Encapsulated in N-Doped Carbon Nanostructures for Efficient Oxygen Reduction Reaction

even though no chemical catalysis is involved. Interestingly, the IUPAC definition of a catalyst is “a substance which increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction” [36]. So, this attempt by IUPAC at a general definition encompassing both homogeneous and heterogeneous reactions perhaps suggests that the same solid particles presenting a greater surface area can be viewed as true catalysts. That said, IUPAC are not necessarily always right, very conspicuously in the curious definition of pH in terms of single ion activities which the IUPAC Gold book asserts “cannot be measured independently,” even describing its own definition as “notional”!

We next turn to RRDEs. In the context of the ORR, these are often used, as introduced by Nekrasov and Frumkin [2], to assess the electrode reaction taking at the disc electrode which is typically made of a candidate electrocatalyst material often synthesized in particulate form. The current–voltage signal is used to assess the amount, if any, of hydrogen peroxide formed on the disc and hence to establish the relative amounts of the 2-electron pathway (forming hydrogen peroxide) as compared to the 4-electron pathway resulting in water where no ring signal is seen in the latter case. This is a good procedure in the case where the disc and ring are co-planar and both flat with zero porosity. However, in the case that the disc, as often happens, is made of a porous or partially porous composite of particles then the criticisms articulated above in respect of using KL analysis again apply. Moreover, the rate at which hydrogen peroxide is released from the porous layer into the solution will reflect transport into and out of the layer which in turn is sensitive to the size, shape, and packing of the particles within the composite, as described by Kätelhön et al. in a series of papers [37–41]. Thus, a *quantitative* assessment of the relative extent of the two processes is likely to be an unrealistic undertaking, although if significant ring currents attributable to hydrogen peroxide are seen then the *qualitative* inference of a significant 2-electron pathway is reasonable. It is evident that a significant appreciation and application of physical electrochemistry is required for

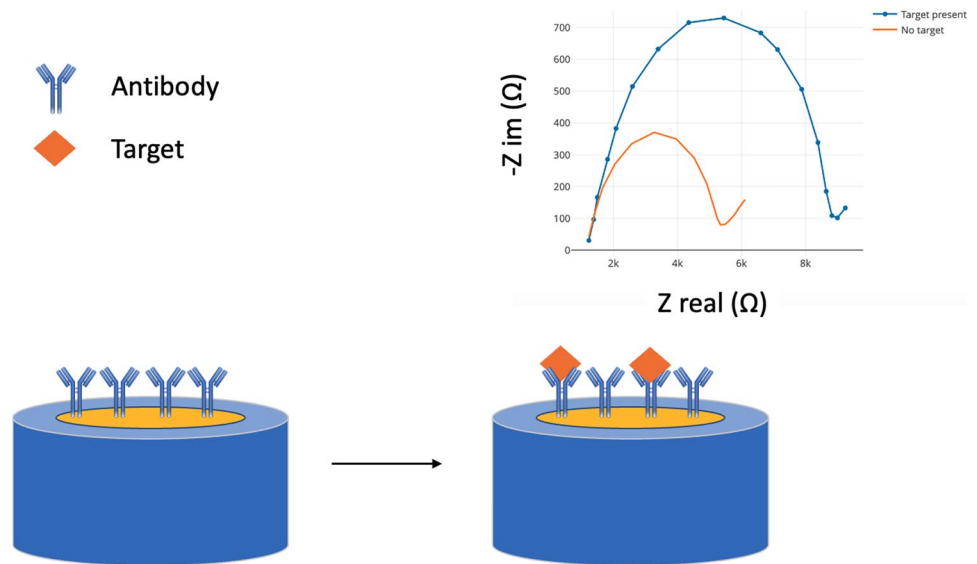
these measurements. The significant consequences, qualitative and quantitative, of ignoring the differences between surface roughness, porosity, and catalysis in the case of the oxidation of hydrazine using palladium nanoparticles [42–44].

We next, as a second example, consider the use of electrochemical impedance spectroscopy (EIS) by non-experts in the field of biological detection. Unlike the use of potential sweeps in RDE and RRDE experiments, EIS involves perturbing the system close to equilibrium using an alternating potential (typically < 20 mV) and observing how the system responds as a function of frequency [45]. Due to the relatively low cost of modern potentiostats and the apparent simplicity of EIS method, the approach became an easy entry point for groups interested in exploring electrochemistry and developing high-sensitivity sensors [46, 47]. The authors claim exquisite levels of sensitivity and selectivity (for example 0.01 ng/ml LoD for PSA detection in phosphate buffer [48], 0.05 ng/ml for the detection of aflatoxin B1 [49], just to name a few) with numerous works published every year. Unfortunately, it is highly uncommon to see independent validation of these startling results.

There are multiple approaches which utilize electrochemical impedance which could be separated into two broad categories: Faradaic and non-Faradaic EIS [50]. Here, we focus on Faradaic EIS which involves the use of redox active mediator(s) and operating at a potential close to the redox couple equilibrium [45]. The predominantly employed procedure requires the use of reversible redox active couple involving a single electron transfer, measuring the impedance of the system at a range of frequencies and performing Randle’s equivalent circuit analysis to determine the value of the charge transfer resistance  $R_{ct}$ .

A typical biosensor involves modification of electrode with a sensing layer which can typically be an antibody or an aptamer receptors [51] to grant specificity and selectivity of detection. The modification method typically involves chemical coupling through utilization of self-assembled monolayers (SAMs) and

**Fig. 3** Faradaic EIS biosensing with an antibody functionalized electrode



standard EDC-NHS chemistry [52]. The modified electrode is then placed into solutions with the absence of target, and charge transfer resistance ( $R_{ct}$ ) is measured. Upon the immersion of the electrode into solutions containing different concentrations of the antibody target molecule, binding takes place which can block the electron transfer and potentially result in change of  $R_{ct}$  value. Calibration curves can be constructed by changing the concentration of the target and then measuring the change in  $R_{ct}$ , thereby enabling one to measure the unknown concentration of the target. The process is shown schematically in Fig. 3.

The great majority of the studies to date have utilized the potassium ferro/ferricyanide couple due to the low cost of the chemicals and ease of experimental setup. The standard potential of the redox couple is such [53] there is no need to degas the solution with an inert gas as the potential is outside the oxygen reduction window. As a result, the experimental setup is greatly simplified as it is conducted under ambient conditions. However, there are key problems associated with the use of this couple. First, the couple is not truly reversible on many electrodes including gold, platinum, and carbon as demonstrated by the work of Xiong et al. among others [54–56]; consequently, the developed theory does not strictly apply. Second, the interfacial process is very sensitive to the surface of the electrode and any modification process makes the results difficult to interpret and to reproduce. The Ferro/Ferri couple is not truly inert and during EIS, it forms a layer of Prussian Blue on gold surfaces (gold is typically used for such experiments) which results in an observed drift of the charge transfer resistance over time as reported by Lazar et al. [57]. The way experiments are performed often involves calibration by increasing concentrations of the solution and subsequent extrapolation of the limit of detection (LoD) value. Consequently, the observed drift can be confused with the signal resulting in spurious measurements.

It is notable that to the best knowledge of the authors there are no large-scale commercial biosensors utilizing EIS for biosensing, except for hematocrit determination in whole blood, despite the apparent maturity of the technique (20+ years of research) and the availability of low-cost apparatus.

In conclusion, we note that electrochemical experiments of interest in applications are almost invariably much more complex than the model systems used to develop and generate experimental techniques. For this reason, we discourage the “off the shelf” approach presently adopted by many. In order to *successfully* realize the true vast potential of electrochemistry in solving energy problems and challenges in chemical sensing, the involvement of expert, trained electrochemists at the heart of the research is essential. Conspicuous limitations to date arguably reflect the over-involvement of amateurs!

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