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Perspective: What constitutes a quality paper in electroanalysis?

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Introduction

Electrochemistry is a core fundamental and multidisciplinary science which is utilised in a plethora of disciplines within the physical, biological and chemical sciences. As electrochemistry is primarily concerned with electron transfer, it is a fundamental part of science and it is widely accepted that the electron is a catalyst [1]. Electrochemistry is the backbone of many applications such as energy storage (batteries and supercapacitors), energy transformation (fuel cells, redox flow and solar cells), corrosion, electrosynthesis, the chloralkali industry, electroanalysis and, of course, sensors.

Within electrochemistry, electron transfer occurs at the electrode|solution interface and the electrode can be considered a giant molecule which is an ideal catalyst with which to undertake oxidation and reduction reactions. Most importantly, the electrochemical reactivity of the electrode is readily controlled by changing the potential difference at the electrode|solution interface. The electrochemical rate constant, k_c , for a reduction process ($A + e^- \xrightarrow{k_c} B$) obeying the Tafel Law is given by:

$k_c \propto \exp\left(\frac{-\alpha FE}{RT}\right)$ where α is the transfer coefficient (~ 0.5), E is the electrode potential, R is the universal gas constant, T is the temperature and F is the Faraday constant. From this fundamental relationship, it can be readily deduced that a change in the electrode potential by ~ 0.5 V can produce a change in k_c by a factor of $\sim 10^5$. As stated by Albery [2] “*Thus with a twitch of a their little finger the electrochemist can alter rate constants through many orders of magnitude*”. This sensitivity of the electrode potential upon the electrochemical rate constant is what dominates the kinetic behaviour of electrochemical processes. This exponential relationship can be thought of similarly to the sensitivity of rate constants to

changes in temperature as described by the Arrhenius equation. Some selected key authoritative textbooks for interested readers to pursue electrochemistry further are as follows: [2–8]

A key area of electrochemistry is that of Analytical Electrochemistry, known widely as *electroanalysis*, which can be considered as the application of electrochemical processes to measure the quantity of a species of interest. The field is substantial, with electroanalytical science widely used in medical diagnosis, environmental monitoring, food and drink safety, athletic performance tracking and a wide-range of biosensors. Electroanalysts are always searching for that next best electrode material. Trends in material science usually dictate the current trends, for example, when my (corresponding author) PhD supervisor was undertaking their DPhil it was buckyballs, when it was my DPhil, carbon nanotubes were all the rage, along with nanoparticle modified electrodes, and then when it was some of my students time, it was 2D materials such as graphene and now new materials such as MXenes are being pursued. Trends move forward but we can learn from our past exploits and the advantages of each need to be clearly articulated, rather than just using them because they are in vogue.

So, *what constitutes a quality paper?*

So, you have finally obtained all your laboratory data, or you think you have. Writing a paper is good way to determine if that is the case, or more data needs to be obtained/repeated/refined. The fact that you have started this journey, is brilliant and a great step forward. In this perspective, we try and provide some feedback, from our limited experiences, of “*what constitutes a quality paper in electroanalysis*”. Below you will find our key points in *italics* with more quantification, detail and answers to help those planning to submit quality papers in the field

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known as electroanalysis. Let's consider some issues/pointers that may, hopefully, help you in your endeavour.

Novelty

This of course should have been explored prior to the experiments/research plan being conducted. There are two broad types of papers that are, in our view, novel. The first is the case of fundamental articles that report new electroanalytical sensing platforms or processes, a new material/electrode composition and/or the first measurements of a new analyte. The second is taking a known electroanalytical method that moves the prior reported fundamental electroanalytical platform further and offers a noteworthy improvement, or new results on an important analyte. It is probably unwise to measure extensively reported electroanalytical targets such as caffeine, ascorbic acid etc. unless you are using these probes as model analytes with which to demonstrate your new fundamental output.

Choice of journal

Your work will fit into a large proportion of journals that will accept electroanalytical based research; but where do you begin? Start by thinking of what type of article you will be writing, what key messages you want to relay and the audience you want to reach. The journal destination will also depend on the novelty of your research. Importantly, read the scope of the journal; this gives an indication of the areas of research the publication and most importantly its readers are focussed on. If you do not meet the scope, the paper will, most likely, be instantly rejected.

Wherever your paper ends up, the main point is that it has been submitted, gone through rigorous peer-review, has probably improved in the process and now the global community can read your latest and greatest. Note that it is no good working on scientific ideas if it remains contained within your laboratory book, the field needs to evolve, and scientific publishing helps this. A point about journal impact factors. The value of a journal's impact factor should not be considered the be-all and end-all; impact factors will rise and fall like the Roman Empire and good published science, irrespective of where it is published, will be found and widely cited by the field. This leads to the Latin phrase: *Non Dficere*, which you should have in-mind when submitting papers, not all get accepted first time. Use the response from the editor/referee's to improve your paper further and re-submit.

Literature

Make sure you have researched the literature thoroughly. Do not just look at papers that were published in journals with high impact factors, that came from large/famous research groups or even indeed potential referees. Instead, cite the research that is relevant to your narrative and those who started your particular field off in its journey. That said, keep the introduction to the point, we are not looking for a mini-review squeezed into an introduction. Clear, concise writing that points to key historical works relevant to your manuscript allows readers to delve deeper into the topic as they wish, whilst also highlighting why your work is a significant step forward in the field.

Experimental section

It is a given this is populated correctly so others can utilise chemicals/materials that you have used, however, this is not always the case. Pay special attention to this to ensure full details are given, this section should enable the reader to recreate your research with an identical outcome. In some cases, it has been reported impurities can dominate nanomaterials. This was not known at the time of those reporting experiments using those materials but having full details in your experimental section will allow further research to build upon your work, go back and check the samples/batches you used and identify the problem more fully allowing the field to progress. Remember that electroanalytical chemistry is trying to provide solutions to significant problems around the globe; as such, working together to explore, understand and

improve procedures is in everyone's best interest. This can only be achieved through honest, well-reported experimental conditions.

Figures

Many argue that the start to writing a paper is with the figures. Make use of the Extra Supporting Information section to ensure that there are not endless figures. It is vital to provide enough data to ensure your conclusions are well-supported, however your manuscript should provide this story eloquently and succinctly. Multi-image figures are useful, allowing double or quadruple the amount of information to be presented to the reader. This can be especially useful when all parts of a figure are related, for example on material characterisation. It is important not to combine multiple figures that are unrelated or not referred to in the text, this can cause confusion on the readers part. Additionally, pay significant attention to the colours used in images, as certain combinations can cause readers more problems than others. Finally, ensure axis/legends are easily readable and not overcrowded, it should be quick and easy to understand what the plot is supposed to be showing.

Title

Try and keep titles to the point, reflecting one or two maximum key findings. For example, avoid overly long and excessive titles such as: "An aptasensor for myoglobin based on the aggregation-induced electrochemiluminescence of nanocubes prepared from a cyclometallated platinum complex and poly(4-vinylpyridine-co-styrene) deposited on nitrogen-doped few layer graphene" Is the key information that you have developed an aptasensor for that specific marker, or that you have made a new complex, or your just deposited this stuff onto graphene – what is the key take home message? Try and keep the title short and concise – the abstract is there to provide full details, not the title.

Electrode area

In all cases, you will have an electrode that is the basis of the electroanalytical platform. It might be modified with new electrocatalytic material, or it may be a completely new electroanalytical platform in itself. For electroanalysts globally to repeat your experience, benchmarking of the electrochemical area is essential. Providing your electroanalytical platform meets the criteria, [9], the use of the appropriate Randles-Ševčík equations can be used to determine A_{real} the electroactive area, which are as follows for reversible, quasi-reversible and irreversible electrochemical processes: [9–11]

$$I_{p,f}^{rev} = \pm 0.446 nFA_{real}C \sqrt{\frac{nFD\nu}{RT}} \quad (1)$$

$$I_{p,f}^{quasi} = \pm 0.436 nFA_{real}C \sqrt{\frac{nFD\nu}{RT}} \quad (2)$$

$$I_{p,f}^{irrev} = \pm 0.496 \sqrt{\alpha n'} nFA_{real}C \sqrt{\frac{nFD\nu}{RT}} \quad (3)$$

where n is the number of electrons in the electrochemical reaction, $I_{p,f}$ is the voltammetric current (analytical signal) using the forward peak of the electrochemical process, F is the Faraday constant ($C \text{ mol}^{-1}$), ν is the applied voltammetric scan rate ($V \text{ s}^{-1}$), R is the universal gas constant, T is the temperature in Kelvin, A_{real} is the electroactive area of the electrode (cm^2) and D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), α is the transfer coefficient (usually assumed to be close to 0.5) and n' is the number of electrons transferred before the rate determining step. Through the use of Eqs. (1)–(3) the electroactive area (A_{real}) can be determined through a simple cyclic voltammetry experiment using a suitable redox probe [9] via a plot of the forward peak current, $I_{p,f}$, as a function of applied voltammetric scan rate ($\nu^{1/2}$). It is also useful to relate A_{real} to that of the geometric area of the electrode, A_{geo} , via: $\%Real = (A_{real} / A_{geo}) \times 100$. For metallic based and related modified electrodes, it is more suitable to measure A_{real} via the use of cyclic voltammetry in an acidic solution, for

example, it is well-known that platinum gives rise to characteristic voltammetric signatures in sulfuric acid solutions. Through the charge consumed in adsorbed hydrogen oxidation, measured by the integration of the voltammetric peaks in the hydrogen region or by chronopotentiometry, A_{real} can be determined; full details can be found at: [12]. It is also useful to be mindful of thin-layer effects [3,13], which can operate when electroanalysts use modified electrodes, such as in the case of carbon nanotubes [13]. In some cases, your modified electrode is porous and electroactive species can be trapped in between the multi-layer layers. It will give the false impression of “electrocatalysis” where it would seem that in comparison to the unmodified electrode, the electrochemical potential of the redox species has shifted to lower overpotential; this is routinely reported as the modifier to be “electrocatalytic”, where in actual fact all that has change is the mass transport from that of a semi-infinite diffusion model (unmodified electrode) to that of a thin layer diffusion model (modified electrode) [3,13]. From the cyclic voltammetric experiment, as detailed earlier to determine A_{real} , a plot of $\text{Log } I_{p,f}$ vs. $\text{Log } \nu$ will be close to 0.5 for semi-infinite diffusion and above 0.5–1.0 for that of thin layer. This should also be reported in papers. Last, the heterogeneous electron transfer rate constant k_{eff}^0 , also be reported.

Amperograms

This is where the sensitivity of the electroanalytical approach is increased, which lowers limits of detection and limits of quantification. Amperograms involve holding the potential at a suitable oxidising or reducing value relative to your electroanalytical target and the current is monitored as a function of time as injections (concentrations) of the target analyte are added and importantly solution is under forced convection, which could be a hydrodynamic technique or simple stirring with a magnetic bar, with the electrode directly above. W. John Albery¹, a doyen of British electrochemists, reports for the case of amperometric sensors where the mass transport is NOT controlled, the current, i , is given by the Albery equation: [8,14]

$$i = f[N_w L(dUGC / dt)]$$

where N , is the number of windows open in the laboratory, L is the number of lorries (trucks) passing outside the laboratory and $dUGC/dt$ is a complicated periodic function describing the visitations of the University Grants Committee (UGC). Of course, “UGC” can be replaced with many comical versions such as with visitations from the Vice-Chancellor or Health and Safety / ethics committee! The way to overcome this is to isolate your experimental set-up as routinely performed in controlled settings (away from external environmental factors) or introduce forced convection, known as hydrodynamic voltammetry, such as using a rotating-disc electrode; for example, this is commonly used during the deposition step, such as in anodic stripping voltammetry. As mentioned above, amperograms are commonly utilised which hide a multitude of

¹ Albery originally presented this equation in his authoritative textbook on Ring-Disc electrodes written with Hitchman, see Ref. [8] Albery. To describe a flawed undergraduate experiment in the Physical Chemistry Laboratory, Department of Chemistry at the University of Oxford which described the current, i , as: $i = f [W, N_i, \partial(JD/\partial t)$ where W is the number of windows open in the laboratory, N_i is the number of lorries passing in South Parks Road and $\partial(JD/\partial t)$ is a complicated periodic function describing the supervision of a typical junior demonstrator. Albery’s work provides characteristically insightful and comical accounts, which is as expected coming from a theatrical family. Albery’s humour is exemplified when asked how Univ’s (University College Oxford) students might wish to address him. “Some of you will feel most comfortable saying ‘Good morning, Master’. Others will prefer ‘Good morning, Professor Albery’. For my part I should like to be greeted with ‘Hello, Sailor’.” Albery’s obituary is a worthy read of this intellectual giant and college antics, such as the “Iron Duke punch” that is named after the ship (HMS Iron Duke) that was regularly served at Univ’s chemistry dinners.

sins and authors are encouraged to provide details on how they perform their experiments, with more details on flow rate and experimental set-up to provide repeatability across the field.

Real sample/interferents

This really depends on the type of paper you have, either a fundamental or new, more applied approach. In the former it is likely that real samples are unlikely to be performed and rather the paper is demonstrating a concept. That said, it would be useful for authors to go that bit further and explore interferents, even in model (buffer) solutions. In the case of a known electroanalytical method that moves the prior reported fundamental electroanalytical platform further offering a noteworthy improvement, the work should undertake interferent studies in model solutions and also in real samples. Ideally, this should be independently validated against a laboratory based standard, e.g. HPLC-UV or UV-VIS etc to demonstrate the robustness of your methodology. This not only helps emphasise the significance of your work, but allows readers of your manuscripts not as well versed in electroanalytical methodologies to fully trust the findings. It may also help convince external funders to push your technology toward commercialisation.

Last, a *table of comparisons*, it is good practice to benchmark your electroanalytical output, if possible, with other previous reports. This is to demonstrate the novelty and a useful table will detail the electrode used, surface composition, (e.g. 2D nanomaterials or nanoparticles) linear range, limit of detection / limit of quantification and sensitivity and any sample matrixes the sensor was tested in which will demonstrate the competitiveness of your sensor. This table will allow you to not only benchmark your sensor in terms of electroanalytical performance but also allow you sell the novelty, e.g. quicker analysis, better sensitivities, cheaper, applied to new samples etc.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Craig E. Banks holds a personal chair in nano- and electrochemical technology and has published over 500 papers (*h*-index: 77, Aug 21) and works on next generation screen-printed electrochemical sensing platforms as well the use of additive manufacturing in water splitting, sensor design, supercapacitors and battery development.



Robert D. Crapnell achieved both his MChem and Ph.D. from the University of Hull, United Kingdom, respectively, in 2014 and 2018. He worked as a PDRA for 18 months and is currently a technical specialist at Manchester Metropolitan University, United Kingdom. His research is predominantly focussed on fundamental electrochemistry, electrochemical, and thermal biosensor development, molecularly imprinted polymers, and additive manufacturing