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Voltammetric Demonstration of Thermally Induced Natural Convection in Aqueous Solution

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In electrochemical systems imperfect thermostating inevitably leads to the presence of bulk convective flows. As recognised by Nernst [Z. Phys. Chem. (1904) 52] damping of these bulk convective flows next to a solid surface, or at the electrode, leads to diffusional mass transport predominating locally. This work questions the exclusivity of diffusional transport and provides hitherto unexplored physical insights into how thermally induced flows in bulk solution can, on both macro- and microelectrodes, influence a voltammetric measurement. Imperfect thermostating results in flows in the bulk solution which are predicted and here expeimentally shown to be of the order of 100 μm s^{-1}. Here we show that even in the absence of natural convective flows induced by the electrochemical reaction itself, this thermally induced bulk convection can significantly affect the voltammetric response. First, evaporative losses from an open electrocehmical cell can be sufficent to produce convective flows that can alter the electrochemical response. Second, electrodes with various sizes and geometries have been investigated and experimental results evidence that the sensitivity of an electrode to these flows in bulk solution is to a large extent controlled by the size of the surrounding non-conductive supporting substrate used to insulate parts of the electrode.

Introduction

Voltammetry lies at the very centre of the study of electrode reactions and, as well as being key to understanding catalysis and analysis, it offers a plethora of fundamental insights across a diversity of problems. Regardless of whether potential steps, sweeps[1] or pulses[2] are used, the current-voltage behaviour is generally interpreted on the basis of a signal in which the mass-transport is controlled exclusively by diffusion except when forced convection is introduced either by flowing the solution or rotating or vibrating the electrode. However, even in the absence of deliberately imposed convection, so-called natural convection can arise. As clarified by Levich[3] one mechanism by which this *may* arise is due to forces originating from the heterogeneous reaction and relate to changes in solution density in the proximity of the reaction surface. Levich[3] identified two cases that can induce a density change, namely first, the intrinsic exo- or endothermicity of the electrode reactions locally altering the solution temperature and second, the local changes in chemical composition induced by the electrolysis causing altered local densities. Levich[3] describes such density driven motion, arising from the occurrence of a heterogeneous reaction, as 'spontaneous' and implicit in these cases is the presence of a gravitational field.[3]

The effect of these reaction driven density changes have been quantified and in the cases of the former (reaction enthalpy induced convection)[4] shown to be negligible, fundamentally reflecting the order of magnitude faster transport of heat as compared to mass, a phenomenon which is restrictively limiting in the case of deliberately heated electrodes as pioneered separately by Wang, Flechsig, Grundler, Baranski and Marken[5-13] for electroanalysis. The situation in which the effects of changes in chemical composition cause density differences (reaction molar volume induced convection) and hence convective flows which augment transport by diffusion has been modelled, for example by Tschulik et al.[14] This latter case is shown to possibly contribute noticeably as compared to edge effect for horizontal macroelectrodes relative to gravity field at times greater than ca. 30 seconds in chronoamperometry when performed in aqueous solution. However, the magnitude of this effect reflects the change in the molar volume during the course of the reaction, the concentration of the electroactive species and the orientation of the electrode relative to the direction of the gravitational field.[15]

Beyond reaction enthalpy and reaction molar volume induced convective flow as described above, another important physical phenomena is that of electro-osmotic flow.[16] Such flows may be induced by applying an electric field in

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perpendicular direction to a double-layer. These flows have important technological applications in microfluidic devices; however, they are of less direct relevance to electro-analytical systems and hence will not be considered further in this work.

When theoretically analysing the influence of electrochemical reaction induced convection (i.e. enthalpy or molar volume induced convection) it is common in electrochemical simulations[14] to presume the presence of a stagnant *bulk* solution. Such a situation requires a uniform temperature throughout the cell. This assumption has recently been questioned and the simulation of typical electrochemical cells using finite element methods has shown the existence of significant flows in bulk solution.[17, 18] These flows can arise from imperfect thermostating of a solution which is, at least to some extent, intrinsic to the concept of maintaining a cell at a fixed temperature within surroundings of different and variable temperatures. A common situation is that an electrochemical cell is immersed in a thermostated water bath but also exposed to the air which may be of a different temperature and/or allow evaporation from the water bath itself. Moreover if the thermal conductivity of the wall in contact with the electrolytic solution is spatially heterogeneous then local differential thermal conduction can lead to local solution phase flows near the glass/solution interface inside the electrochemical cell. Furthermore and in particular, evaporation of solvent from the surface of the liquid contained in the cell locally reduces the temperature and can cause significant flows. These flows are driven by the local temperature differences causing changes in the solution density. The consequence of these effects is that even in the absence of other extrinsic forces (such as vibrations) the bulk solution contains natural convective flows; due to imperfect thermostating an aqueous solution will tend not towards a quiescent state but a convective stationary one with a non-zero flow velocity. The question arises as to the extent to which these density induced convective flows can influence voltammetry?

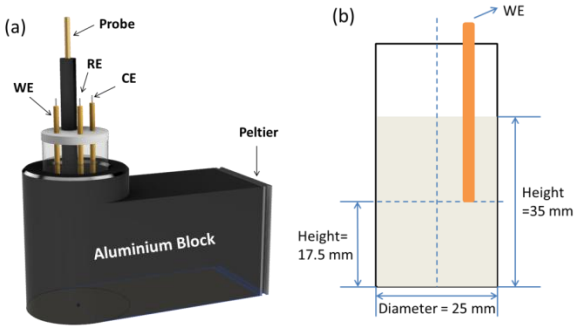
Experimental

Chemical Reagents

The ferrocenemethanol ($FcCH_2OH$; ChemCruz) and potassium chloride (KCl; Sigma-Aldrich; ≥ 99.0%) were used as purchased without further purification. Solutions (1 mM $FcCH_2OH$ in 0.1 M KCl) were prepared using deionised water (Milipore) with a resistivity of 18.2 MΩ cm.

Instrumentation

Electrochemical measurements were performed with a µAutolab Type III using a standard three electrode setup in an optimised thermostated electrochemical cell as shown in Scheme 1 (a). The detail of this design was described in the previous paper[19]. A saturated calomel electrode (SCE; BASi, Japan) and a silver wire were used as reference electrode and counter electrode, respectively. Four different electrodes were used as working electrodes as mentioned below. All experiments were conducted in a glass vial (Specimen tubes soda glass, 50 × 25 mm, SAMCO) containing 12 mL of solution (1 mM $FcCH_2OH$ in 0.1 M KCl) except where otherwise stated. The side view of the set-up of the vial is shown in Scheme 1(b), in this system the electrodes were positioned horizontally facing downward and at a height equal to half of the solution depth. Details regarding experiments performed with the electrode in different orientations relative to the gravitational field are detailed further in the SI Section 1.



Scheme 1 (a) Schematic of the optimised thermostated electrochemical cell. The probe is used to sense the temperature of the electrochemical cell, which is controlled by a Peltier. (b) Schematic of the side-view of the set-up within the glass vial. WE, RE and CE represent the working electrode, reference electrode and counter electrode, respectively. The surface of working electrode shown here is horizontal facing downward.

Electrochemical Measurement

Electrode Design Four different electrodes were used as working electrodes: conventional carbon fibre microcylinder electrode (7 µm in diameter), and commercial carbon fibre micro tip electrode (7µm in diameter; Carbonstar-1, Kation Scientific), commercial carbon microdisc electrode (33 µm in diameter; BASi) and commercial glassy carbon macroelectrode (3 mm in diameter; BASi). Prior to experiments, the latter two electrodes were polished using alumina of decreasing size (1.0, 0.3 and 0.05 µm, Buehler, IL, U.K), washed with deionised water and dried with nitrogen.

Thermostating measurements All voltammetric measurements were carried out at 25.0 °C within both a closed cell and an open cell. The cyclic voltammetry was scanned from -0.1 V to 0.5 V at a scan rate of 25 mV s^{-1} except where otherwise stated. For the experiments in an open cell, the measurements were taken every 15 mins.

Simulation software The commercially available simulation software DigiSim® is used to simulate the one-dimensional (1D) diffusion only models, for example planar, (hemi-)cylindrical, (hemi-)spherical geometries. This simulation is based on a fully implicit finite difference (IFD) algorithm suggested by Manfred Rudolph[20-22] and it allows simulations for a wide range of mechanisms.

Results and discussion

We recently reported the design and application[19] of an optimised thermostated cell with minimised vibration and thermal effects which was well-characterised by means of both experimental and computational modelling to describe the extent to which the full thermostating of a cell by a heated bath can be realised. The modelling included heat transfer due to evaporation and radiative processes and, in agreement with experiments, indicated that the steady-state temperature of the cell could deviate from that of the thermostat by ~0.1 K. Such a spatial inhomogeneity of the temperature is predicted to drive convective flows of speed of the order of 100 μm s^{-1} in bulk solution.[19]

Chronoamperometric responses on a macrodisc electrode

First, the oxidation of a model redox probe under these *relatively* quiescent conditions is studied in the electrochemical cell schematically shown in Scheme 1. Figure 1 shows the chronoamperometric response of a glassy carbon macro-electrode (3 mm in diameter) towards the oxidation of 1 mM ferrocene methanol up to a time of 60 seconds. In this experiment the working electrode is facing downward, as would be most commonly done in an electroanalytical experiment. Overlaid is the theoretical time current transient as predicted using a) the Cottrell equation[1] and b) the Shoup-Szabo equation.[23] The Shoup-Szabo equation additionally accounts for the contribution of radial diffusion towards the macrodisc electrode. Excluding the first 0.3 seconds of the experiment where capacitative charge is important, over the course of the rest of the experiment the measured current deviates from the theoretical results by an average of 1.4%, as shown in the inlay of Figure 1. In this system, with a downward orientation of the electrochemical interface and in which external causes of convection have been minimised the macro-electrode response can (within the uncertainty of the reported diffusion coefficient and electrode dimensions) be fully and accurately described by a diffusion only model.

An important question is to what extent may the orientation of the electrode effect this result? SI Section 1 outlines more details regarding experiments performed with other macroelectrode orientations. Briefly the results show that for the present experimental case (1mM ferrocene methanol aqueous solution with 0.1 M KCl) only in the situation in which the electrode is vertical (perpendicular to the gravitational field) is there an appreciable effect on the electrochemical response. As the electrochemical reaction proceeds it induces a change in density of the solution adjacent to the electrochemical interface causing convective flows. In the case of a vertically orientated electrode this results in the mass-transport limited current being 10% greater than predicted current on the basis of Shoup-Szabo equation[23] (See SI Section 1 for more detail). The influence of such electrochemical reaction induced convection will lessen as the size of the electrode decreases[15]. Consequently, the above 10% increase in current for a vertically orientated macroelectrode represents, in this work, a likely largest possible contribution for natural convection induced by the occurrence of the interfacial reaction. Hence, in the remainder of this work we continue by only considering the voltammetric contribution associated with bulk convection arising from thermal differences in the cell.

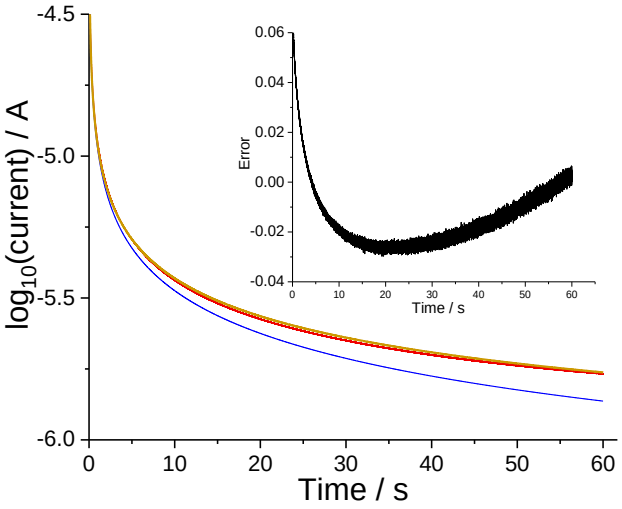


Figure 1: The experimentally recorded chronoamperometric response of a glassy carbon macrodisc electrode (red) (r = 0.15 cm) plotted against that predicted on the basis of the Cottrell (blue) and Shoup-Szabo equations (brown). Inlay in (a) depicts the error between the experimental (red) and simulated chronoamperometric response that predicted by the Shoup-Szabo (brown) see SI Section 2 for more details. The excellent agreement of the experimental data with the Shoup-Szabo equation highlights the importance of accounting for radial diffusion at this time scale even when using an electrode of millimetres in dimension. The experiment was run in a glass vial with 12 mL solution (1 mM $FcCH_2OH$ in 0.1 M KCl) at a constant applied potential of +0.35 V with the macroelectrode facing downwards.

Cyclic voltammetry on microcylinder electrode in an open cell

We now turn to use a less 'conventional' electrode design; that of a micro-cylinder electrode. The reason for this choice will be evidenced later in the text. Figure 2 presents the voltammetric response of carbon fibre microcylinder electrode (diameter = 7.0 μm and length 0.92 mm) towards the oxidation of ferrocene methanol (1 mM) at a scan rate of 25 mV s^{-1}. The microcylinder electrode is an interesting geometry for voltammetric experiments where, as is the case for band electrodes, due to the electrode being macroscopic in one dimension under diffusion only conditions the voltammogram does not reach a true steady state flux and in the mass-transport limit the current varies with the inverse of log time; this leads to a peak shaped voltammogram.[24] Prior to recording the cyclic voltammograms presented in Figure 2 the cell was thermostated to 25°C and allowed to equilibrate for a period of ca. 10 minutes. For a 'closed' voltammetric cell (one sealed to avoid evaporative losses) then the voltammetric response of the electrode was invariant with time (see SI Section 3) and found to be within experimental error of that predicted for a diffusion only system (the simulated diffusion

only response for this electrode is overlaid with the data in Figure 2). Conversely for the same electrode submerged in an 'open' cell (one in which the solution is free to evaporate), although the initial voltammetric scans are equivalent to that measured in a closed cell, at longer times ca. 45 minutes the voltammetric wave shape is altered and the current at high-overpotentials (in the mass-transport limited region) increases. This increase in the current indicates that a process other than diffusion is contributing to the mass-transport limited flux of material to the electrode surface. By considering the magnitude of the increase in current to the micro-cylinder electrode shown in Figure 2, we can estimate that the solution phase velocity is of the order of 10 μm s^{-1} after 60 minutes.[25]

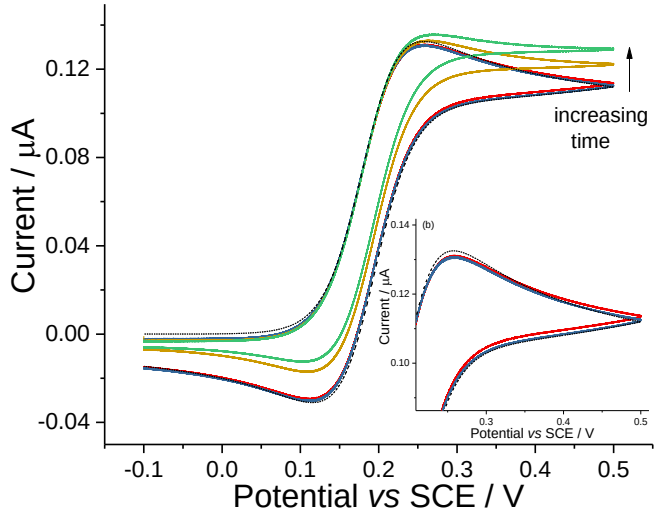


Figure 2 The oxidation of ferrocene methanol (1 mM) at 25 °C at a carbon fibre micro-cylinder electrode (d= 7.0 μm, l = 0.92 mm) as a function of time in a cell open to the environment at times after the cell has been brought to temperature, 25 minutes (blue), 45 minutes (brown), 60 minutes (green). The experimental voltammogram in a closed cell (red) and the simulated result (black dashed line) are also depicted for comparison. Inlay shows the zoom-in version of the comparison between the simulated voltammogram (black dashed line) and the experimental results. The experiment was run in a glass vial with 12 mL solution (1 mM $FcCH_2OH$ in 0.1 M KCl) at 25 mV s^{-1}.

Although a crude estimate this rate of flow is comparable to that previously predicted for bulk flows in this cell associated with thermal gradients induced by evaporative losses. This conclusion that evaporation is leading to bulk convective flows and that it is these bulk flows that are altering the voltammetric response is evidenced by the fact that the change in the voltammetric response is only observed when the cell is open to the environment. Consequently, we conclude evaporative losses from a cell can significantly influence the voltammetric response by changing the mass-transport. The SI Section 4 briefly explores the manner in which vibrations may also similarly affect the voltammetric behaviour of the micro-cylinder electrode.

It is useful at this stage to consider some results previously presented in the literature. Amatore et al.[26, 27] reported experiments conducted in a cell (a microscope petri dish) with no thermostating and which was 'open' to the environment allowing evaporative losses. In their work chronoamperometry was semi-empirically modelled using a distance dependent effective diffusion coefficient (which scaled with the 4th power of the normal distance from the electrode surface)[28]. First, the magnitude of the reported distance dependent diffusion coefficients allow the back calculation and estimation of the speed of the convective eddies, these estimates are consistent with the magnitude for the flow simulated as described above.[4, 29] Second, the work explicitly did not consider the influence of radial diffusion on the chronoamperometric response and at least 50% of their 'measured' discrepancy can be understood on the basis of a diffusion only mass-transport model which fully accounts for this additional flux (see SI Section 5). Further work in the literatute[30] suggests that beyond forced and density (aka gravitationally) driven convection an additional microscopic convection model needs to be considered to understand natural convection in electrochemical systems. We note however that first, "a spontaneous excitation of internal convection cannot be generated from a state at rest in a system which is at thermodynamic equilibrium",[31] the 'spontaneous' natural convection discussed by Levich[3] arises due to the occurrence of an electrochemical reaction i.e. it is induced by the system being in a non-equilibrium state. Moreover, the experimental results we present in Figure 1 clearly demonstrate that for the electrode orientation used relative to the gravitational field (downward), analyte identity and concentration and, where external influences such as vibrations and non-perfect thermostating have been minimised, then over a timeframe of 60 seconds at a macro-electrode, no other mass-transport mechanism need be invoked to explain the results. Furthermore nor do distance dependence diffusion coefficients represent physical reality but merely attempt to parameterise the transition from stagnant to density driven convection zone. The results shown in Figure 2 demonstrate how convection can be induced to occur, due to the influence of the external environment on the cell causing evaporative losses.

It is on the basis of such literature experiments[26, 30] into convection that a categorisation of electrodes as either being 'microelectrodes' or 'ultra-microelectrodes' has been previously proposed.[32] Zonal diagrams were produced to reportedly define the behaviour of an electrochemical system. Succinctly it was suggested that larger electrodes are more sensitive (in terms of their measured voltammetric response) towards natural convection than smaller ones. Here we ask, to what extent is this generally true?

Effect of natural convection on different electrode geometries

In order to reproducibly and controllably create a density gradient in the electrochemical cell the system was first thermostated and allowed to equilibrate. Having attained a near quiescent system the thermostat temperature was increased by one degree Celsius. In the present experimental system a peltier heat pump is used to control the thermostat

temperature. This temperature jump method will necessarily induce convective flows in the electrochemical cell which are likely of the order of 1 mm s^{-1}.[19] Figure 3 presents the recorded voltammetric response for four different electrode types towards the oxidation of ferrocene methanol prior to (red line) and immediately after (blue line) the onset of the temperature jump. Over the course of the voltammetric experiment the solution phase temperature, as recorded in-situ by a thermocouple, was raised by approximately one degree Celsius, note however, under these conditions the solution phase temperature in the cell is heterogeneous. Figure 3 a) and b) present the voltammetric responses for a macroscopic (d=2.98 mm) and a microscopic (d = 33 µm) disc electrode where both electrodes are inlaid in a non-conductive support (support diameters of 6.0 and 3.5 mm). The voltammetric response of neither electrode is particularly altered by the change in the systems thermostating or hence the induced convection. Conversely Figure 3 c) and d) depicts the voltammetric response of a carbon fibre microcylinder electrode and a carbon fibre micro tip electrode. Importantly the carbon fibre electrode (Figure 3 d) is only surrounded by a thin glass sheath (~0.4 µm). The various electrode geometries used are outlined schematically in Figure 3. The voltammetric responses of both electrodes (c and d) are markedly altered by the change in the thermostating conditions. Moreover, the increase in the mass-transport limited current cannot be rationalised in terms of the diffusion coefficient of ferrocene methanol. For a one degree Celsius change in the solution temperature the diffusion coefficient of ferrocene methanol is only anticipated to increase by ca. 2.5 %.[33]

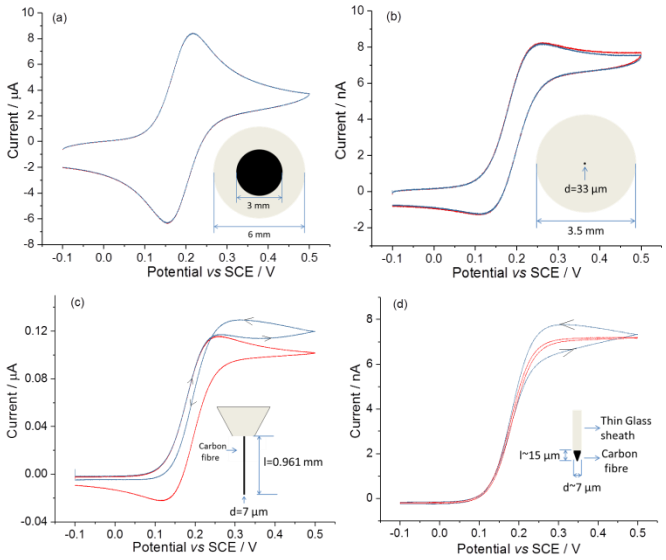


Figure 3: Effect of temperature change on the voltammograms for (a) macroelectrode, (b) commercial carbon microdisc electrode, (c) carbon fibre microcylinder electrode and (d) carbon fibre tip electrode. Macroelectrode used in (a) is glassy carbon electrode with a diameter of 3 mm. Commercial carbon microdisc electrode used in (b) is 33 µm in diameter. The carbon fibre used in (c) and (d) are 7 µm in diameter. The red curves represents for the voltammograms at a constant temperature (20 °C), and the blue curves represents for the voltammograms at each electrode with a temperature jump. Inlays in each figure represent the schematic of each electrode. The experiments were run in a glass vial with 12 mL solution (1 mM $FcCH_2OH$ in 0.1 M KCl) at 25 mV s^{-1}.

The above results directly point to the importance of the electrode surround in altering the convective profile near the electrode which influences the mass-transport environment local to the electrochemical interface. The solution phase velocity at a solid surface is necessarily zero (no slip boundary) and a microelectrode inlaid in a relatively large glass sheath is essentially shielded from the bulk convective flows. Microelectrodes that are inlaid in non-conductive glass sheaths are less sensitive to bulk convective flows as compared to macroelectrodes (that are also inlaid in a non-conductive surface). This however does not mean that microelectrodes are inherently immune to such flows; it is the non-conducting support structure that creates a larger stagnant layer adjacent to the electrochemical interface. The notion of a bulk solution in which there is significant mixing, promoted by density differences, and which is separated from a surface by a stagnant diffusion layer is of course the physical basis for the simple Nernst diffusion layer model dating from 1904.[34] But the above results demonstrates more broadly that this stagnant layer thickness is sensitive to the local environment; the mass-transport to and from a point on a non-reactive surface will, in terms of the influence of convection, differ from that of an isolated point in solution.

It is important to recognise that microelectrodes that are not encased in large insulating surfaces are routinely used in electrochemical experiments. Such electrodes are often employed for example as probe electrodes in scanning electrochemical microscopy (SECM) and other analytical contexts. Consequently, if such 'unsheathed' microelectrodes are in bulk solution then depending on the local convective environment the measured steady-state current may differ significantly from that of a diffusion only model. This has two potential implications first, the accurate calibration of such electrodes may be challenging. Second, in experimental setups where the electrodes distance from an interface is varied, such as an approach curve, the influence of convection on the measured electrochemical response will vary as a function of the electrode/surface separation. Therefore, the careful and rigorous[35] thermostating of electrochemical systems using such unsheathed microelectrodes is a likely necessary requisite.

In summary, convection in electrochemical systems can significantly influence the voltammetric response. Generally convection is classified as either forced or natural. Forced convection induced by deliberate flowing, vibrating or rotating of the electrode is a routinely used method to enhance the rate of mass-transport to an electrochemical interface. However, in the absence of deliberately induced convection it is common for an electrochemical system to be interpreted solely on the basis of a diffusion-only model. However, there are a number of mechanisms that may still lead to the convective movement of the solution in an electrochemical

cell. First, there may be sources of external adventitious forced convection, a prime example being vibrations arising from the laboratory environment. Such unintentional sources of forced convection can be, as is done in this work, often easily and sufficiently minimised by firmly securing the cell and damping local vibration sources. More complex is the issue of so-called natural convection. Natural convection is a broad term encompassing a number of physical phenomena. Generally natural convection refers to gravitationally driven convection resulting from local density differences in the solution. As outlined by Levich[3] such density differences may be driven by the occurrence of the electrochemical reaction itself, arising either due to the reaction enthalpy or molar volume change associated with the electrochemical reaction.

Conclusions

In this work we use only millimolar concentrations of the electroactive analyte and demonstrate experimentally that for the used orientation of the electrode the influence of natural convection induced by the change in enthalpy or the reaction molar volume of the electrochemical reaction itself only contributes minimally to the present experimental case. Consequently, having minimised and controlled all other sources of forced and natural convection this allows us to investigate to what extent thermally induced natural convection can be important in such voltammetric measurements. We demonstrate how imperfect thermostating of an electrochemical cell can and does lead to significant density driven convective flows. These convective flows may influence an electrochemical response of a system by altering the mass-transport regime. This convection can be driven simply by the evaporative loss of solution from an electrochemical cell which is open to the environment. The use of distance dependent diffusion coefficients to model the effects of convection in an electrochemical cell, as employed in the literature, is cautioned against on both a theoretical[31] and experimental basis.

Importantly, we show how the sensitivity of an electrode towards convective flows in the bulk solution is not just a function of the electrodes size but is also importantly influenced by the size and geometry of the non-conductive support surrounding the electrode. The sensitivity of a microelectrode towards bulk convective flows is less if the electrode is inlaid into a large macroscopic surface. The surrounding substrate serves to shield the electrode and creates a larger stagnant layer near the reactive interface. This highlights a general insight that unsheathed microelectrodes i.e. ones that are not embedded in a large non-conductive support surface are generally more sensitive to solution phase convection. This has potential implications for a variety of experimental systems that used such unsheathed electrodes; highlighting a source of irreproducibility that is generally not considered.

Conflicts of interest

There are no conflicts to declare.

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