Effect of heterogeneity on the dc and ac voltammetry of the $[\text{Fe(CN)}_6]^{3-/4-}$ solution-phase process at a highly ordered pyrolytic graphite electrode

Chong-Yong Lee$^a$, Si-Xuan Guo$^a$, Alan M. Bond$^{a,*}$, Keith B. Oldham$^{b,*}$

$^a$ School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
$^b$ Department of Chemistry, Trent University, Peterborough, ON, Canada K9J 7B8

Received 29 May 2007; received in revised form 26 November 2007; accepted 27 November 2007
Available online 4 December 2007

Abstract

The effect of surface heterogeneity in dc and ac voltammetries has been investigated with a variety of dual-electrode materials and electrode reactions for quasi reversible electron-transfer reactions in which the substrate and product are present as solutes. Typically, and as theoretically expected, when two distinctly different surfaces are present, the faradaic currents arising from each region combine additively. This leads to a marked effect on the shape of the transient response, particularly in the ac voltammetric case. However, heterogeneity is not possible to detect when the rate constants for the two regions are identical in magnitude (or reversible). At the other extremity where very large differences in rate constants occur, it is possible to detect fully resolved voltammetric process. For example, the presence of a small region of edge planes on an otherwise highly ordered pyrolytic graphite electrode surfaces clearly reveals itself in the case of $[\text{Fe(CN)}_6]^{3-}$ electro-reduction. In this example, the vastly enhanced reversibility of the electron-transfer at defect sites present in the edge planes, compared with the much slower reaction on the highly ordered pyrolytic graphite surface leads to detection of two well resolved $[\text{Fe(CN)}_6]^{3-/4-}$ processes from an experiment at a single electrode.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Kinetic dispersion; Electrode heterogeneity; dc cyclic-voltammetry; Large-amplitude ac voltammetry; Highly ordered pyrolytic graphite electrode

1. Introduction

The complex subject of voltammetry at spatially heterogeneous electrodes has been reviewed recently by Compton and co-workers [1]. These authors had previously employed digital simulations to investigate the implications of electrode heterogeneity in a wide range of scenarios. In the present context, a “heterogeneous electrode” is one whose surface consists of two (or more) regions, differing in composition and/or structure. These differences lead to distinct electrochemical behaviour in each region, the measured response being a combination of the two. Heterogeneity of an electrode might arise from an adsorption occurring on part of the original surface, from the presence of surface oxides, from different crystal orientations, from surface topography, from inclusions in or detritus on the surface, or even from deliberate electrode design [2]. Clearly, the unrecognized presence of heterogeneity can lead to erroneous conclusions or faulty data, if the response is analyzed on the false assumption of surface homogeneity. The earliest mentions [3,4] of electrochemical anomalies attributable to electrode heterogeneity appeared in the 1950s, and the topic has been current in the electrochemical literature ever since [1,5–18].

An important special case of electrode heterogeneity occurs when one of the two regions lacks electrochemical activity entirely. Such electrodes are described as “partially blocked” and they have been the subject of much research...
In the more general case, in which electron exchange occurs on both regions, it is possible for quite different reactions to take place on the two types of surface (as with many corrosion scenarios), or the same reaction via different mechanisms. More usually a single reaction occurs on both regions, though under different kinetic regimes, and this is the happenstance with which this document is concerned. As noted by Compton and co-workers [1,15], one must expect that each region will have its own standard rate constant ($k^0_1$ in region 1, $k^0_2$ in region 2), a state of affairs to which the term “kinetic dispersion” applies. The charge transfer coefficients, $\alpha_1$ and $\alpha_2$ also might differ. In the present study we address only electrode reactions that may be represented by

$$S(\text{soln}) - ne^- \rightarrow P(\text{soln})$$

in which both the substrate and product are soluble in the electrolyte solution. In such cases, a single standard potential $E^0$ must apply to both regions, because the same difference $\Delta G^0$ in Gibbs free energy drives the reaction at both sites. However, in instances where one or both of $S$ and $P$ are adsorbed or surface confined, different standard potentials will likely be encountered. In such cases, not addressed here, both kinetic dispersion and “thermodynamic dispersion” is to be expected.

A variety of electrochemical techniques, including rotating disk voltammetry, chronoamperometry, cyclic-voltammetry, chronopotentiometry and impedance spectroscopy, has been employed in studies of electrode heterogeneity [1,5–18]. The research described here involves experimental studies with cyclic-voltammetry and the Fourier method. We use “the Fourier method” as a convenient abbreviated designator of the Fourier-transform-inverse-Fourier-transform large-amplitude-sinusoidal-potential-modulated harmonically analyzed cyclic-voltammetry method, that has been developed in this laboratory in recent years [19–25]. This method is advantageous in the present studies because of its demonstrated selectivity [23–25], particularly in the higher harmonics, to the reversibility of the electrode process and, of course, kinetic dispersion often makes its presence felt as a perturbation of the reversibility of the electron-transfer.

In order to understand the implications of heterogeneity in voltammetry, the surface of a heterogeneous electrode can be imagined to consist of a mosaic of two regions, sharing a total area $A$. If subscripts “1” and “2” are introduced to distinguish the two regions, then the symbols $\theta_1$ and $\theta_2$ (equal to $1 - \theta_1$) denote the fractions of the total area occupied by each region. When there is equal coverage by the two regions, each $\theta$ equals one-half.

In order to address this inherently complex problem theoretically, it is possible (see, for example, [5] or [1]) to adopt a model geometry in which the more-active region consists of sites of specific geometry (disks, strips, microhemispheres) separated by a contiguous “sea” of the less-active region. Alternatively, and perhaps more realistically, the electrode surface may be viewed as a mosaic in which the two regions are not distinguished topologically or specified geometrically and hence simply intermingle in some random way. The mosaic under these conditions will have a “graininess” associated with it, and this graininess can be characterized by a length parameter $A$. For our present purpose, a precise definition of $A$ is not needed, but it could be defined, for an electrode composed of two regions, as the total electrode area divided by the total length of the interregional boundary. $A$ may range from atomic dimensions, as for an electrode composed of a metallic alloy, to a size comparable with that of the electrode itself, as for the dual electrodes used in the initial experiments described in later sections.

Two extreme geometries may be recognized, according to how the length-scale $A$ compares in size to the diffusion layer thickness, which can be taken as $\sqrt{\pi Dt}$. A situation that will be termed macroheterogeneity exists if $A \gg \sqrt{\pi Dt}$. Conversely, if $A \ll \sqrt{\pi Dt}$ one has microheterogeneity. The intermediate situation, in which $A$ and $\sqrt{\pi Dt}$ are of comparable length, will be described as mesoheterogeneity. Because the diffusion layer generally increases in size during a voltammetric experiment, the degree of heterogeneity may change too.

The physics of what happens is fundamentally different among the three cases. With microheterogeneity, there is a single concentration profile, common to the entire electrode. Macroheterogeneity results in two distinct profiles, the one adjacent to the region 1 being different from that adjacent to region 2, with negligible interaction between the two. In the mesoheterogeneity case, the regions are distinct but the zone in which the profiles mutually interact is considerable, leading to significant transport parallel to the electrode surface, a circumstance that does not lend itself to facile analysis. This situation has been considered by Compton and co-workers [1].

Let us first address macroheterogeneity. In this case it is as if we have two independent electrodes, one of area $\theta_1A$ for region 1 and one of area $\theta_2A$ for region 2. In electrical parlance, the two component electrodes are “in parallel”. The measured current is the sum of currents from each region, proportional to $[(\theta_1A)k^0_1 + (\theta_2A)k^0_2]c^{\text{ch}}$ for this macroheterogeneous case.

Now consider microheterogeneity. In this case a molecule (or ion) of substrate S, diffusing towards the electrode “doesn’t know” whether it will encounter region 1 or region 2. The probability is $\theta_1$ that the molecule will react at region 1, whereas there is a $\theta_2$ probability of electrons being exchanged with region 2. The fraction $\theta_1$ of the diffusing molecules will experience a rate constant of $k^0_1$, the remainder will react with a rate constant of $k^0_2$. The net effect is as if there were two distinct substrates codiffusing towards the electrode and reacting there at different rates; one with a bulk concentration of $\theta_1c^{\text{ch}}$ and destined to encounter rate constant $k^0_1$, the other with a bulk concentration of $\theta_2c^{\text{ch}}$ that will experience a rate constant of $k^0_2$. Again, the current will be the sum of the two, proportional to $A[(\theta_1c^{\text{ch}})k^0_1 + (\theta_2c^{\text{ch}})k^0_2]$ in the general microheterogeneous case.
Because the terms \( [(\theta_1A)k_{01}^h + (\theta_2A)k_{02}^h]e^h \) and \( A[(\theta_1e^h)k_{01}^h + (\theta_2e^h)k_{02}^h] \) are mathematically identical, one concludes on the bases of this simplified form of analysis, and in conformity with the conclusions of Compton and co-workers [1], that there is no distinction between outcomes for macroheterogeneity and microhomoogeneity. However, the predicted identity of results for micro- and macroheterogeneity does not imply that the heterogeneity has no effect. On the contrary, as Compton and co-workers showed for a specific model [1], kinetic dispersion has a profound effect on the shape and other characteristics of voltammograms.

Mesoheterogeneity cannot be analyzed so simply, though a treatment by Compton and co-workers [1] throws light on this intermediate situation. Qualitatively, one would certainly expect that mesoheterogeneity will cause a mild increase in the total current. Clearly, if the electrode reaction is reversible on both regions, the rate constants and transfer coefficients disappear from the modeling. In this event, the effect of heterogeneity is undetectable voltammetrically. With other degrees of reversibility, there is hope of detecting heterogeneity in the voltammogram, though this will be challenging unless \( k_{01}^h \) and \( k_{02}^h \) are sufficiently dissimilar.

Experimentally, as noted above, electrode heterogeneity may be encountered in many circumstances, but needs to be detected as part of quantitative analysis of an electrochemical problem. In this study, we have used initially a series of dual-electrode configurations with a variety of electrode processes of variable level of reversibility to ascertain the ease of detection of the impact of heterogeneity under different scenarios. In particular this series of model studies reveals the high sensitivity of detection of heterogeneity by the Fourier method. We then concluded our experimental study by demonstrating the impact of heterogeneity in the case of a single electrode configuration by showing how two fully resolved processes may readily be detected if the rate constants pertaining to regions on the electrode surface are sufficiently different.

2. Experimental section

2.1. Chemicals

Acetonitrile (HPLC grade, Merck) was dried over molecular sieves prior to use. In this solvent, \( [(n-C_4H_9)_4N][PF_6] \) (GFS Chemicals) served as supporting electrolyte after twice being recrystallized from ethanol. The acetylacetone complex of cerium(IV), \( \text{K}_3[\text{Fe(CN)}_6] \) (Aldrich), respectively. from \( [\text{Ru(NH}_3)_6]^3^+ \) and \( [\text{Fe(CN)}_6]^3^- \) electroactive species were derived either from \( [\text{Ru(NH}_3)_6]^3^+ \) (Strem Chemicals) or from \( [\text{Co}^{2+}][\text{PF}_6] \) (GFS Chemicals) served as supporting electrolyte.

2.2. Electrodes

A static mercury drop dispenser (Bioanalytical Systems) was used for studies utilizing a mercury electrode. This device delivers drops of reproducible areas in several sizes, that numbered “9” was chosen for use in this study, the corresponding area being 1.67 mm\(^2\). A highly ordered pyrolytic graphite electrode was prepared from “ZYH grade” material (Advanced Ceramics Corporation, Wales) by cleaving the surface with adhesive tape. Heterogeneity was introduced by hand polishing with ethanol-wetted tissue paper, or by cleaving with the sharp tip of a glass pipette. After rinsing with distilled water, the graphite electrode was mounted into a custom-made Perspex cell where it was held in position with an O-ring and Perspex screws, which exposed an area of 38 mm\(^2\). The edge-plane pyrolytic graphite electrode was fabricated by adhering a small square piece of edge-plane pyrolytic graphite to a brass rod with silver loaded epoxy adhesive (RS Components), and then placing this into a Teflon sheath and embedding it in epoxy resin. After being dried, the electrode was sanded with dry and wet silicon carbide paper (1200 grit) to remove the possible adherence of epoxy on electrode surface. Other working electrodes (Bioanalytical Systems) were a 1.6 mm diameter gold electrode (Au), a 1.6 mm diameter platinum electrode (Pt) and two distinct glassy carbon disk electrodes (GC1 and GC2), each of 3.0 mm diameter. Prior to use in voltammetric experiments, each of the electrodes was polished with an aequous 0.3 μm alumina suspension on a polishing cloth (Buehler), rinsed with water, then sonicated to remove excess alumina, before a final rinse with water and drying in nitrogen.

The auxiliary electrode was a platinum wire. For aqueous solutions an Ag/AgCl/NaCl(3 M) reference electrode was employed. For experiments in acetonitrile solvent, the reference electrode was a silver wire in a CH\(_3\)CN solution of 0.10 M \([n-(C_4H_9)_4N][PF_6]\) and 0.01 M AgNO\(_3\). Two frits separated the reference and working chambers.

Dual electrodes, simulating macroheterogeneity, were prepared simply by connecting two single electrodes in parallel and dipping the conjoined pair into the cell. Care was taken to configure the two working electrodes and the auxiliary electrode into an isosceles triangular arrangement, to minimise unbalanced resistances.

2.3. Apparatus

Conventional dc cyclic-voltammetric experiments were carried out using a Bioanalytical Systems (West Lafayette, Indiana) model 100B Electrochemical Workstation. Experiments employing the Fourier method were performed with apparatus described elsewhere [22]. A standard three-electrode cell was employed in all electrochemical measurements.
2.4. Procedures

The areas of the gold (1.98 mm\(^2\)), platinum (2.08 mm\(^2\)), glassy carbon (7.02 mm\(^2\)) and edge-plane graphite electrodes (1.36 mm\(^2\)) were determined from measured peak heights of potential-scan voltammograms for the one-electron reversible reduction of 1.00 mM \([\text{Fe(CN)}_6]^{3-}\) in 0.10 M aqueous KCl solution. The known diffusivity \(D = 7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}\) was employed [27]. Areas of the mercury drops were determined in a similar way, except that the reduction of \(\frac{1}{2} [\text{Ru(NH}_3)_6]^{3+}\) (with \(D = 6.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}\) [27]) was substituted as the electrode process.

The cobaltocenium/cobaltocene reduction wave was used as an internal reference in establishing the potential scale for voltammetry in acetonitrile [28].

Table 1

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Scan rate (mV s(^{-1}))</th>
<th>(\Delta E_p) (mV)</th>
<th>(\frac{(E_p^{\text{red}} + E_p^{\text{ox}})}{2}) (V)</th>
<th>(\frac{j_{p}^{\text{red}}}{j_{p}^{\text{ox}}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (Hg)</td>
<td>50</td>
<td>69</td>
<td>-0.44</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>70</td>
<td>-0.44</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>68</td>
<td>-0.45</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>72</td>
<td>-0.45</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>63</td>
<td>-0.45</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>66</td>
<td>-0.45</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>69</td>
<td>-0.44</td>
<td>1.07</td>
</tr>
<tr>
<td>Glassy carbon (GC1)</td>
<td>50</td>
<td>83</td>
<td>-0.44</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>82</td>
<td>-0.44</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>83</td>
<td>-0.44</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>96</td>
<td>-0.44</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>96</td>
<td>-0.44</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>97</td>
<td>-0.44</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>103</td>
<td>-0.44</td>
<td>0.98</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>50</td>
<td>170</td>
<td>-0.46</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>205</td>
<td>-0.46</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>238</td>
<td>-0.46</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>268</td>
<td>-0.47</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>296</td>
<td>-0.47</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>326</td>
<td>-0.47</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>352</td>
<td>-0.48</td>
<td>0.95</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>50</td>
<td>235</td>
<td>-0.47</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>246</td>
<td>-0.47</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>275</td>
<td>-0.47</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>331</td>
<td>-0.47</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>360</td>
<td>-0.48</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>383</td>
<td>-0.48</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>403</td>
<td>-0.48</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The charge transfer coefficient, \(\alpha\), was assumed to be 0.5 in all simulations.

Table 2

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Concentration of (\alpha-\text{[Ce(acac)}_4]) (mM)</th>
<th>Rate constant, (k^0) (10(^{-5}) m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (Hg)</td>
<td>0.70</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>381</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>401</td>
</tr>
<tr>
<td>Glassy carbon (GC1)</td>
<td>0.70</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>113</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>0.70</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>19</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>0.70</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 1. Cyclic-voltammograms obtained for the reduction of 1.00 mM \([\text{Ru(NH}_3)_6]^{3+}\) in 0.10 M aqueous KCl solution at a scan rate of 52 mV s\(^{-1}\) using the GC1 (---) and a GC2 (-----) electrodes individually, and the GC1 + GC2 dual-electrode (—).

Fig. 2. Cyclic-voltammograms obtained for reduction of 1.00 mM \([\text{Co(p-C}_5\text{H}_5}_2]^{3+}\) in acetonitrile (0.10 M \([\text{n-C}_4\text{H}_9\text{N}][\text{PF}_6]\)) at a scan rate of 52 mV s\(^{-1}\) using Au (---) or Hg electrodes (-----) individually, and the Hg + Au dual-electrode (—).
All voltammetric experiments were undertaken at 20 ± 1 °C and the solutions were degassed with high-purity nitrogen for at least 5 min prior to the electrochemical experiments in order to remove oxygen.

Assignment of standard rate constants from cyclic-voltammetric data was made with assistance from and DigiElch or DigiSim [29] software.

## 3. Results and discussion

### 3.1. Cyclic-voltammetry

Prior to the study of heterogeneity, we validated the concept of dual-electrode voltammetry by analyzing many experimental results, exemplified by those shown in Fig. 1. This displays conventional cyclic-voltammograms under the conditions specified in the figure legend for the reduction of 1.00 mM \( [\text{Ru}(\text{NH}_3)_6]^{3+} \) in 0.10 M aqueous KCl solution at a scan rate of 52 mV s\(^{-1}\). Of the three curves, one was obtained from the single GC1 electrode, the second from the GC2 electrode and the third from the dual GC1 + GC2 electrode. In appearance, only two curves are evident because the first and second curves exactly overlie each other, as they should because GC1 and GC2 are identical in area. The third curve, from the dual-electrode, appears to be of twice the size as the others, and precise measurements show this to be almost exactly the case. Again, this is just as expected.

We expect that heterogeneous electrodes, including the dual electrodes by which we simulate heterogeneity, will behave differently from those in Fig. 1, because of kinetic dispersion arising from the distinct kinetic behaviour of the various electrode materials. We therefore carried out

---

**Fig. 3.** Cyclic-voltammograms obtained at a scan rate of 1000 mV s\(^{-1}\) for the reduction of 0.60 mM \( \alpha-[\text{Ce}(@)\text{acac}4] \) in acetonitrile (0.10 M \( [\text{n-C}_4\text{H}_9]_4\text{N}[\text{PF}_6] \)) using a GC (---) or a Pt electrode (···), and the GC + Pt dual-electrode (—). In diagram (a), the ordinate is current; in (b) it is current density.

---

**Fig. 4.** Cyclic-voltammograms obtained for the reduction of 1.00 mM \( [\text{Fe(CN)}_6]^{3-} \) in aqueous 0.10 M KCl solution at a scan rate of 75 mV s\(^{-1}\). (a) HOPG electrode shows highly irreversible process, (b) HOPG electrode with edge-plane defect sites displays both a reversible and an irreversible process.
preliminary studies to demonstrate that, indeed, our individual electrodes do behave diversely under the conditions of cyclic-voltammetry. Table 1 summarizes the results of 28 experiments, all undertaken on the reduction of 0.70 mM $\alpha$-[Ce(acac)$_4$] in acetonitrile with 0.10 M [(n-C$_4$H$_9$)$_4$N][PF$_6$] as the supporting electrolyte. The values listed for the peak-to-peak separation, and its dependence on scan rate, clearly point to the reduction being most reversible on mercury and declining in reversibility in the sequence Hg > GC > Au > Pt. The third column, listing the mean of the reduction and oxidation peak potentials, $(E_{\text{red}}^p + E_{\text{ox}}^p)/2$ versus Fc/Fc$^+$, suggests either a minor dependence of this value on the reversibility or, more likely, the presence of a small level of systematic error inherent in this commonly used method of estimating the reversible standard potential. Nevertheless, the average value is close to previously reported values [26,30]. The measured peak-height ratios, reported in the final column of Table 1, are all within 10% of the expected unity value. In view of the subjectivity in measuring $I_{\text{ox}}^p$, we regard this as satisfactorily in accord with standard cyclic-voltammetry theory [27].

To employ cyclic-voltammetry as a trustworthy method of making quantitative measurements of electron-transfer rate constants, one must measure consistent values, not only at a variety of scan rates, but also at several concentrations. Otherwise, there is a danger of failure to detect the possible influence of uncompensated resistance on the results. Data collected with this caveat in mind are presented in Table 2. They quantify the reversibility trend observed in Table 1.

Fig. 2 shows three cyclic-voltammograms for the reduction of the cobaltocenium cation $[\text{Co}((^5\text{C}_5\text{H}_5)_2)]^{+}$ at a concentration of 1.00 mM in an acetonitrile solution containing 0.10 M [(n-C$_4$H$_9$)$_4$N][PF$_6$]. The electrodes were Au, Hg, and the dual Au + Hg electrode. Once again, as expected, the current at the dual-electrode for a process that is reversible at both electrode surfaces is the sum of the currents at the individual electrodes even though, in this case, the voltammograms of the single electrodes are quite different from each other.

Single electrodes are again compared with the corresponding dual-electrode in the cyclic-voltammograms.
shown in Fig. 2 for the quasireversible reduction of \(\alpha-[\text{Ce(acac)}]_3\). In this case, the greater reversibility at glassy carbon, compared with platinum is clear, but nevertheless the additivity of the component currents is evident in diagram 3a. In diagram 3b, the data have been processed to remove the effect of the different electrode areas. The intermediary of the apparent reversibility of the dual-electrode, between those of the two single electrodes, is apparent.

Great irreversibility is implied by the extreme peak splitting observed in the cyclic-voltammograms for the reduction of the \([\text{Fe(CN)}_6]^{3-}\) ion in aqueous solution at a highly ordered pyrolytic graphite. Observe in the diagram in Fig. 4a that the irreversibility is so extreme that a central region has developed in which there is no current. Fig. 4b, was obtained from the same highly ordered pyrolytic graphite electrode that had been deliberately maltreated, as described in Section 2.2, in an attempt to introduce some edge planes defect sites, thereby creating a heterogeneous electrode. This attempt evidently succeeded because the central region is now occupied by a “mini-cyclic-voltammogram” arising from reduction at the edge planes, which are known [31–35] to foster much faster electron exchange than the basal planes of highly ordered pyrolytic graphite.

McCreery and co-workers reported freshly cleaved highly ordered pyrolytic graphite occasionally exhibited double voltammetric peaks which corresponded to a high defect density [34,35].

3.2. The Fourier method

Two voltage signals are applied to the working electrode in what we here call “the Fourier method”. One of these signals is identical to the forward-then-reverse ramps that are standard in cyclic-voltammetry. The second is a sinusoidal signal of constant amplitude and frequency that modulates the ramps. In the experiment reported here, the sinusoidal signal usually had an amplitude of 80 mV, a frequency of 9.98 Hz and the ramp rate was between 44 mV s\(^{-1}\) and 75 mV s\(^{-1}\).

The current generated by the twin signal is subjected to Fourier transformation. This splits the current into a number of components, each with a “real” and an “imaginary” segment. After filtering out unrequired frequencies and inverse Fourier transformation, these segments at the frequencies of interest are combined vectorially (the square-root of the sum of the squares) to regenerate the amplitude.

![Diagram](image-url)
of the corresponding current component. The fundamental (or “first harmonic”) component is that portion of the current that shares the same frequency, \( \omega \), as the applied sinusoid. There are second, third, fourth, etc. harmonic components that have frequencies of \( 2\omega, 3\omega, 4\omega \), etc., and there is an aperiodic component. The last is often called “the dc component”, but we avoid the “dc” designation to avoid possible confusion with the current recorded in the total absence of sinusoidal modulation. In fact, the aperiodic component frequently resembles a conventional cyclic-voltammogram, but the two are not identical, either experimentally or theoretically.

The results of the Fourier method are presented in the form of a number of diagrams, each depicting one component of the current, and generally displays as graphs of current versus time. However, the aperiodic component is often reported in the “folded” representation customary for cyclic-voltammetry, in which case the abscissa becomes a voltage axis.

With the reduction of the \( \text{Ru(NH}_3)_6^{3+} \) as the electrochemical reaction, the Fourier method was applied first to the GC1 electrode, then to the GC2 electrode and finally to the dual GC1 + GC2 electrode. The results are shown in Fig. 5 as four diagrams representing the aperiodic current and the component currents of frequency \( \omega, 2\omega, \) and \( 3\omega \), where \( \omega \) is the frequency applied sinusoidal voltage. The fourth, fifth and sixth harmonics were also examined, but these are not reported. Results from the dual-electrode are shown by a full line, and those from the single GC electrodes as dashed and dotted lines. Where a diagram appears to show only two curves, this is because the curves for the two single electrodes overlap.

In fact, as expected, there is almost total overlap in most diagrams. Fig. 5b is an exception; in that case there is a significant offset between the ostensibly identical GC1 and GC2 electrodes which suggest that the double layer capacitance at GC2 exceeds that at GC1 by almost a factor of 2. (The background current at GC electrodes strongly depended on polishing and composition of the surface.) Otherwise, the four diagrams show responses by the single electrodes that are typical of almost-reversible electron-exchange reactions. It is known that the second- and higher harmonic response in the Fourier method is insensitive to capacitive background, so it is not surprising that the dis-

Fig. 7. Analysis of the reduction of 0.60 mM \( \alpha\text{-}[\text{Ce(acac)}_4] \) in acetonitrile (0.10 M \( \text{[(n-C}_4\text{H}_9)_4\text{N}]PF_6 \)) by Fourier-transform ac voltammetry. (a) The aperiodic dc component, (b), (c) and (d) the fundamental, second and third-harmonic ac components of Au (---) and Hg electrodes (---), and the Au + Hg dual-electrode (---). Scan rate 44.70 mV s\(^{-1}\), sinusoidal amplitude and frequency, 80 mV and 9.98 Hz, respectively.
crepancy between the responses of GC1 and GC2 is absent in Fig. 5e and d. As expected, the dual-electrode displays a current equal to the sum of the currents from the individual electrodes.

The additivity of signals is again evident in Fig. 6, in which the quartet of diagrams have the same significance as in Fig. 5. Here, however, the individual electrodes are Au (dashed line) and Hg (dotted line), the reaction in question being the reversible reduction of the cobaltocenium cation. The full line relates to the dual-electrode Au + Hg.

Two characteristics of the Fourier method are that the intensity of the response falls off with the harmonic

---

**Fig. 8.** Analysis of the reduction of 1.00 mM [Fe(CN)₆]³⁻ in 0.10 M aqueous KCl solution by Fourier-transform ac voltammetry. 8(a1)–(a3) are the aperiodic dc components, 8(b1)–(b3), 8(c1)–(c3) and 8(d1)–(d3) are the fundamental, second and third-harmonic ac components. 8(a1),(b1),(c1),(d1) for the highly ordered pyrolytic graphite electrode exhibit only a highly irreversible process; 8(a2),(b2),(c2),(d2) for the fully edge-plane pyrolytic graphite electrode displays only a reversible process; 8(a3),(b3),(c3),(d3) for the highly ordered pyrolytic graphite electrode with edge-plane defect site displays both a reversible and an irreversible process. Scan rate 74.51 mV s⁻¹, sinusoidal amplitude and frequency, 80 mV and 9.98 Hz, respectively.
number, while the complexity of the response increases with harmonic number. Generally, the same response occurs during each of the ramps, forward and reverse. These features are evident in both Figs. 5 and 6. Another feature is that there is discrimination against irreversible processes in all the periodic responses, but particularly in the higher harmonics. This property is apparent in Fig. 7.

The response to the Fourier method for reduction of \([\text{Ce(acac)}_4]\) in acetonitrile solution containing 0.1 M \([n-(\text{C}_4\text{H}_9)_4\text{N}]\text{PF}_6\) as supporting electrolyte is depicted in Fig. 7. The electrodes are Au, Hg and the dual Au + Hg electrode. Diagram 7a shows the current at the fundamental frequency \(\omega\), while 7b and 7c portray the harmonic currents at frequencies of \(2\omega\) and \(3\omega\). Notice that, even though the area of the Au electrode is slightly larger than that of the Hg electrode, all three diagrams show a diminished response at the gold electrode compared with the mercury. This correlates with gold’s lower electron-exchange rate constant for this reaction, as in Table 2. In Fig. 7b and c, the current levels are so low that measurement anomalies are to be expected. Thus, we do not believe that the third-harmonic peak currents for the dual-electrode are truly smaller than the sum of the currents for the individual electrodes, as Fig. 7c suggests. Higher harmonics are very sensitive to the ohmic losses, and this may be the origin of this observation.

As just demonstrated, the Fourier method discriminates in favour of reversible processes, especially in the higher harmonics. Thus, it could be predicted that if one of the regions of a heterogeneous electrode shows irreversibility, while the other provides a significantly more reversible electron-transfer, the resulting Fourier voltammogram will reveal the kinetic dispersion. This technique should therefore be an ideal tool for detecting heterogeneity when one of the regions fosters high reversibility. In this aspect, the damaged highly ordered pyrolytic graphite, previously discussed, should provide an ideal surface, because it consists of a large percentage of basal-plane material, offering rather slow electron exchange to the ferricyanide ion, with a smaller admixture of edge-plane graphite, whose defects foster faster exchange.

As described in Section 2.2, a highly ordered pyrolytic graphite electrode was damaged to introduce edge-plane reaction sites. Its ability to facilitate the ferricyanide reduction process, under the conditions of the Fourier method, was then compared with that of an undamaged replica and a fully edge-plane graphite electrode. In Fig. 8, diagrams 8a1, 8b1, 8c1 and 8d1 relate to the undamaged highly ordered pyrolytic graphite electrode; while diagrams 8a3, 8b3, 8c3 and 8d3 were obtained with the damaged electrode. The remaining four diagrams 8a2, 8b2, 8c2 and 8d2 were obtained from the fully edge-plane pyrolytic graphite electrode.

The aperiodic Fourier voltammograms in Fig. 8a1 and a3 are remarkably similar to the classical dc cyclic-voltammograms in Fig. 4a and b. Whereas the undamaged electrode (Fig. 8a1) supports no current in the voltage range 0.0 < \(E\) < 0.3 V, a very small voltammogram, attributable to the edge planes, appears in this range for the damaged electrode (Fig. 8a3). The small separation of the peaks in this minivoltammogram contrasts with the huge peak separation for the basal-plane electrode, confirming that the kinetic dispersion is extreme in this example.

The damaged highly ordered pyrolytic graphite electrode exhibited background capacitive current as the sum from both basal-plane and edge-plane surfaces, where it was clear that the latter contributes the larger proportion. The minimal second-harmonic response, in Fig. 8c1 at times around 10 s and 42 s, suggests that only mild background current arises from an undamaged highly ordered pyrolytic graphite electrode. These times correspond to the voltage range mentioned in the previous paragraph. In contrast, very dominant forward and reverse ac signals were observed at those particular times for the damaged highly ordered pyrolytic graphite electrode (Fig. 8c3). This is attributed to the high kinetic sensitivity of the Fourier method to the reversible reduction of ferricyanide at the edge-plane defect sites. It is clear from Fig. 8c2 that edge planes are responsible for the dominant peaks. The kinetic discrimination becomes even more significant in the third-harmonic response, where the ac signals attributed to the highly irreversible reduction of \([\text{Fe(CN)}_6]^{3-}\) at highly ordered pyrolytic graphite are not detectable (Fig. 8d1). In contrast, at both the damaged (Fig. 8d3) and the edge-plane (Fig. 8d2) surfaces, the fast electron-transfer process generates readily measurable third-harmonic components.

4. Conclusions

For the most part, a heterogeneous electrode delivers a faradaic current that is the weighted sum of the currents from the two regions. However, unless the electrode reaction is reversible on both regions, the shape of the voltammogram will differ from that for a homogeneous electrode. As a result, the analysis of a voltammogram from a heterogeneous electrode as if it were homogeneous will not generally yield meaningful data.

If the rate constants for reaction on the two regions are sufficiently dissimilar, the presence of kinetic dispersion may be recognized from anomalous features in the dc or ac voltammograms. The second and higher harmonics generated by the Fourier voltammetric method are particularly powerful for detecting kinetic dispersion associated with electrode heterogeneity.

Acknowledgements

We thank Barry Fleming, Darrell Elton, Jie Zhang and Jan Myland for generous and valuable assistance. The financial support of the Australian Research Council and the Natural Sciences and Engineering Research Council of Canada is acknowledged with gratitude. C.Y.L. also gratefully acknowledges the award of postgraduate scholarships (MIPRS and MGS) from Monash University.
References