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A Review of Non-Cottrellian Diffusion Towards Micro- and Nano-Structured Electrodes

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1. Introduction

The past few decades have seen a massive and continued interest in studying electrochemical processes at artificially structured electrodes. As is well known, the rate of redox reactions taking place at an electrode depends on both the mass transport towards the electrode surface and kinetics of electron transfer at the electrode surface. Three modes of mass transport can be considered in electrochemical cells: diffusion, migration and convection. The diffusional mass transport is the movement of molecules along a concentration gradient, from an area of high concentration to an area of low concentration. The migrational mass transport is observed only in the case of ions and occurs in the presence of a potential gradient. Convective mass transport occurs in flowing solutions at rotating disk electrodes or at the dropping mercury electrode.

In 1902 Cottrell derived his landmark equation describing the diffusion current, I , flowing to a planar, uniformly accessible and smooth electrode of surface area, A , large enough not to be seriously affected by the edge effect, in contact with a semi-infinite layer of electrolyte solution containing a uniform concentration, c_0 , of reagent reacting reversibly and being present as a minor component with an excess supporting electrolyte under unstirred conditions, during the potential-step experiment (Cottrell, 1902)

$$I = nFAc_0\sqrt{\frac{D}{\pi t}}, \quad (1)$$

where n is the number of electrons entering the redox reaction, F is the Faraday constant, D is the diffusion coefficient, and t is time.

It has long been known that the geometry, surface structure and choice of substrate material of an electrode have profound effects on the electrochemical response obtained. It is also understood that the electrochemical response of an electrode is strongly dependent on its size, and that the mass transport in electrochemical cell is affected by the electrode surface roughness which is generally irregular in both the atomic and geometric scales. Moreover, the instant rapid development in nanotechnology stimulates novel approaches in the preparation of artificially structured electrodes. This review seeks to condense information on the reasons giving rise or contributing to the non-Cottrellian diffusion towards micro- and nano structured electrodes.

2. Electrode geometry

Cottrell equation, derived for a planar electrode, can be applied to electrodes of other simple geometries, provided that the temporal and spatial conditions are such that the semi-infinite diffusion to the surface of the electrode is approximately planar. However, in both the research and application spheres various electrode geometries are applied depending on the problem or task to be solved. Most electrodes are impaired by an “edge effect” of some sort and therefore do not exhibit uniform accessibility towards diffusing solutes. Only the well defined electrode geometry allows the data collected at the working electrode to be reliably interpreted. The diffusion limited phenomena at a wide variety of different electrode geometries have been frequently studied by several research teams. Aoki and Osteryoung have derived the rigorous expressions for diffusion-controlled currents at a stationary finite disk electrode through use of the Wiener-Hopf technique (Aoki & Osteryoung, 1981). The chronoamperometric curve they have obtained varies smoothly from a curve represented by the Cottrell equation and can be expressed as the Cottrell term multiplied by a power series in the parameter \sqrt{Dt}/r , where r is the electrode radius. Later, a theoretical basis for understanding the microelectrodes with size comparable with the thickness of the diffusion layer, providing a general solution for the relation between current and potential in the case of a reversible reaction was given by the same authors (Aoki & Osteryoung, 1984). A user-friendly version of the equations for describing diffusion-controlled current at a disk electrode resulting from any potential perturbation was derived by Mahon and Oldham (Mahon & Oldham, 2005). Myland and Oldham have proposed a method that permits the derivation of Cottrell’s equation without explicitly solving Fick’s second law (Myland & Oldham, 2004). The procedure, based on combining two techniques – the Green’s Function technique and the Method of Images, has been shown to successfully treat several electrochemical situations. Being dependent on strict geometric conditions being met, it may provide a vehicle for a novel approach to electrochemical simulation involving diffusion in nonstandard geometries. In the same year Oldham reported an exact method used to find the diffusion-controlled faradaic current for certain electrode geometries that incorporate edges and vertices, which is based on Green’s equation (Oldham, 2004). Gmucová and co-workers described the real electrochemical response of neurotransmitter dopamine on a carbon fiber microelectrode as a power function, i.e., $\propto t^\beta$ (Gmucová et al., 2004). That power function expanded to the polynomial terms can be, in conformity with (Aoki & Osteryoung, 1981; Mahon & Oldham, 2005), regarded as a Cottrell term, multiplied by a series of polynomial terms used to involve corrections to the Cottrell equation.

The variation of the diffusion layer thicknesses at planar, cylindrical, and spherical electrodes of any size was quantified from explicit equations for the cases of normal pulse voltammetry, staircase voltammetry, and linear sweep voltammetry by Molina and co-workers (Molina et al., 2010a). Important limiting behaviours for the linear sweep voltammetry current-potential curves were reported in all the geometries considered. These results are of special physical relevance in the case of disk and band electrodes which possess non-uniform current densities since general analytical solutions were derived for the above-mentioned geometries for the first time. Explicit analytical expressions for diffusion layer thickness of disk and band electrodes of any size under transient conditions

were reported by Molina and co-workers (Molina et al., 2011b). Here, the evolution of the mass transport from linear (high sizes) to radial (microelectrodes) was characterized, and the conditions required to attain a stationary state were discussed. The use of differential pulse voltammetry at spherical electrodes and microelectrodes for the study of the kinetic of charge transfer processes was analyzed and an analytical solution was presented by Molina and co-workers (Molina et al., 2010b). The reported expressions are valid for any value of the electrode radius, the heterogeneous rate constant and the transfer coefficient. The anomalous shape of differential pulse voltammetry curves for quasi-reversible processes with small values of the transfer coefficient was reported, too. Moreover, general working curves were given for the determination of kinetic parameters from the position and height of differential pulse voltammetry peak. Sophisticated methods based on graphic programming units have been used by Cuttress and Compton to facilitate digital electrochemical simulation of processes at elliptical discs, square, rectangular, and microband electrodes (Cuttress & Compton, 2010a; Cuttress & Compton, 2010b).

A general, explicit analytical solution for any multipotential waveform valid for an electrochemically reversible system at an electrode of any geometry is continually in the centre of interest. This problem has been solved many times (e.g., Aoki et al., 1986; Cope & Tallman, 1991; Molina et al., 1995; Serna & Molina, 1999). A general theory for an arbitrary potential sweep voltammetry on an arbitrary topography (fractal or nonfractal) of an electrode operating under diffusion-limited or reversible charge-transfer conditions was developed by Kant (Kant, 2010). This theory provides a possibility to make clear various anomalies in measured electrochemical responses. Recently, analytical explicit expressions applicable to the transient I - E response of a reversible charge transfer reaction when both species are initially present in the solution at microelectrodes of different geometries (spheres, disks, bands, and cylinders) have been deduced (Molina et al., 2011a).

3. Electrochemical cells with bulk resistance

Mathematical modeling of kinetics and mass-transfer in electrochemical events and related electroanalytical experiments, generally consists of dealing with various physico-chemical parameters, as well as complicated mathematical problems, even in their simplest statement.

An analysis of the transient response in potential controlled experiments is a standard procedure which can yield information about many electrochemical processes and several kinetic parameters. However, a resistance in series (i.e., solution resistance, electrode coating resistance, sample resistance in solid state electrochemistry) can have a serious effect on electrochemical measurements. Thus, the presence of migration leads to essential deviations from the Cottrellian behaviour. Electrochemical systems that exhibit bulk ohmic resistances cannot be characterized accurately using the Cottrell equation. Electrochemical experiments in solution without added supporting electrolyte, i.e., without suppressed migration, became possible with the progress of microelectrodes. The expressions for current vs. time responses to applied voltage steps across the whole system, and corresponding concentration profiles within the cell or membrane were derived by Nahir and Buck and compared with experimental results (Nahir & Buck, 1992). Voltammetry in solutions of low ionic strength has been reviewed by Ciszowska and Stojek (Ciszowska & Stojek, 1999). A mathematical model of migration and diffusion coupled with a fast preceding reaction at a

microelectrode was developed by Jaworski and co-workers (Jaworski et al., 1999). Myland and Oldham have shown that on macroelectrodes the Cottrellian dependence can be preserved even when supporting electrolyte is absent. The limiting current, however, was shown to depart in magnitude from the Cottrellian prediction by a factor (greater or less than unity) that depends on the charge numbers of the salt's ions and that of the electroproduct (Myland & Oldham, 1999). A generalized theory of the steady-state voltammetric response of a microelectrode in the absence of supporting electrolyte and for any values of diffusion coefficients of the substrate and the product of an electrode process was presented by Hyk and Stojek (Hyk & Stojek, 2002).

The influence of supporting electrolyte on the drugs detection was studied and data obtained using cyclic voltammetry, steady-state voltammetry and volt coulometry on the same analyte were compared to each other by Orlický and co-workers. Under unsupported conditions different detection limits of the above mentioned methods were observed. Some species were easily observed by the kinetics-sensitive volt coulometry even for concentrations near or under the sensitivity limit of voltammetric methods (Orlický et al., 2003). Thus, systems obeying deviations from Cottrell behaviour should find their application in sensorics. Later, it has been revealed that the dopamine diffusion current towards a carbon fiber microelectrode fulfills, within experimental errors and for concentration similar to those in a rat striatum, the behaviour theoretically predicted by the Cottrell equation. Nevertheless, under unsupported or weakly supported conditions non-Cottrellian responses were observed. Moreover, markedly non-Cottrellian responses were observed for dopamine concentrations lower or higher than the physiological ones in the rat striatum. It has been also shown, that the non-Cottrellian behaviour of diffusion current involves the nonlinearity of the dopamine calibration curve obtained by kinetics-sensitive volt coulometry, while voltammetric calibration curve remains linear (Gmucová et al., 2004). Similarly, Caban and co-workers analysed the contribution of migration to the transport of polyoxometallates in the gels by methods of different sensitivity to migration (Caban et al., 2006).

Mathematical models of the ion transport regarded as the superposition of diffusion and migration in a potential field were analyzed by Hasanov and Hasanoglu (Hasanov & Hasanoglu, 2008). Based on the Nernst-Planck equation the authors have derived explicit analytical formulae for the concentration of the reduced species and the current response in the case of pure diffusive as well as diffusion - migration model, for various concentrations at initial conditions. The proposed approach can predict an influence of ionic diffusivities, valences, and initial and boundary concentrations to the behaviour of non-Cottrellian current response. In addition to these, the analytical formulae obtained can also be used for numerical and digital simulation methods for Nernst-Planck equations. The mathematical model of the nonlinear ion transport problem, which includes both the diffusion and migration, was solved by the same authors (Hasanov & Hasanoglu, 2009). They proposed a numerical iteration algorithm for solving the nonlocal identification problem related to nonlinear ion transport. The presented computational results are consistent with experimental results obtained on real systems.

The quantitative understanding of generalized Cottrellian response of moderately supported electrolytic solution at rough electrode/electrolyte interface was enabled with the Srivastav's and Kant's work (Srivastav & Kant, 2010). Here, the effect of the uncompensated

solution resistance on the reversible charge transfer at an arbitrary rough electrode was studied and the significant deviation from the classical Cottrellian behavior was explained as arising from the resistivity of the solution and geometric irregularity of the interface. In the short time domain it was found to be dependent primarily on the resistance of the electrolytic solution and the real area of the surface. Results obtained for various electrode roughness models were reported. In the absence of the surface roughness, the current crossover to classical Cottrell response as the diffusion length exceeds the diffusion-ohmic length, but in the presence of roughness, there is formation of anomalous intermediate region followed by classical Cottrell region. Later, the theoretical results elucidating the influence of an uncompensated solution resistance on the anomalous Warburg's impedance in case of rough surfaces has been published by the same authors (Srivastav & Kant, 2011).

4. Modified electrodes

Modified electrodes include electrodes where the surface was deliberately altered to impart functionality distinct from the base electrode. During last decades a large number of different strategies for physical and chemical electrode modification have been developed, aimed at the enhancement in the detection of species under interest. Particularly in biosciences and environmental sciences such electrodes became of great importance. One of the issues raised in the research of redox processes taking place at modified electrodes has been the analysis of changes in the diffusion towards their altered surfaces.

Historically, liquid and solid electrochemistry grew apart and developed separately for a long time. Appearance of novel materials and methods of thin films preparation lead to massive development of chemically modified electrodes (Alkire et al., 2009). Such electrodes represent relatively modern approach to electrode systems with thin film of a selected chemical bonded or coated onto the electrode surface. A wide spectrum of their possible applications turned the spotlight of electrochemical research towards the design of electrochemical devices for applications in sensing, energy conversion and storage, molecular electronics etc. Only several examples of possible electrode coatings are mentioned in this chapter, all of them in close contact with the study of the electron transfer kinetic on them.

4.1 Micro- and nanoparticle modified electrodes

Marked deviations from Cottrellian behaviour were encountered in the theoretical study (Thompson et al., 2006) describing the diffusion of charge over the surface of a microsphere resting on an electrode at a point, in the limit of reversible electrode kinetics. A realistic physical problem of truncated spheres on the electrode surface was modelled in the above mentioned work, and the effect of truncation angle on chronoamperometry and voltammetry was explored. It has been shown that the most Cottrell-like behaviour is observed for the case of a hemispherical particle resting on the surface, but only at short times is the diffusion approximated well by a planar diffusion model. Concurrently, Thompson and Compton have developed a model for the voltammetric response due to surface charge injection at a single point on the surface of a microsphere on whose surface the electro-active material is confined. The cyclic voltammetric response of such system was investigated, the Fickian diffusion constrained on spherical surfaces showed strong deviations from the responses expected for planar diffusion. The Butler-Volmer condition

was imposed for the electron transfer kinetics. It was found that the peak-to-peak separations differ from those expected for the planar-diffusion model, as well as the peak currents and the asymmetry of the voltammetric wave at higher sweep rates indicate the heterogeneous kinetics. The wave shape was explained by the competing processes of divergent and convergent diffusion (Thompson & Compton, 2006). Later, the electrochemical catalytic mechanism at a regularly distributed array of hemispherical particles on a planar surface was studied using simulated cyclic voltammetry (Ward et al., 2011). As is known, a high second-order rate constant can lead to voltammetry with a split wave. The conditions under which anomalous 'split-wave' phenomenon in cyclic voltammogram is observed were elucidated in the above-mentioned work.

In recent years significant attention is paid to the use of nanoparticles in many areas of electrochemistry. Underlying this endeavour is an expectation that the changed morphology and electronic structure between the macro- and nanoscales can lead to usefully altered electrode reactions and mechanisms. Thus, the use of nanoparticles in electroanalysis became an area of research which is continually expanding. Within both the trend towards the miniaturisation of electrodes and the ever-increasing progress in preparation and using nanomaterials, a profound development in electroanalysis has been connected with the design and characterisation of electrodes which have at least one dimension on the nano-scale.

In a nanostructured electrode, a larger portion of atoms is located at the electrode surface as compared to a planar electrode. Nanoparticle modified electrodes possess various advantages over macroelectrodes when used for electroanalysis, e.g., electrocatalysis, higher effective surface area, enhancement of mass transport and control over electrode microenvironment. An overview of the investigations carried out in the field of nanoparticles in electroanalytical chemistry was given in two successive papers (Welch & Compton, 2006; Campbell & Compton, 2010). Particular attention was paid to examples of the advantages and disadvantages nanoparticles show when compared to macroelectrodes and the advantages of one nanoparticle modification over another. From the works detailed in these reviews, it is clear that metallic nanoparticles have much to offer in electroanalysis due to the unique properties of nanoparticulate materials (e.g., enhanced mass transport, high surface area, improved signal-to-noise ratio). The unique properties of nanoparticulate materials can be exploited to enhance the response of electroanalytical techniques. However, according to the authors, at present, much of the work is empirical in nature. Belding and co-workers have compared the behaviour of nanoparticle-modified electrodes with that of conventional unmodified macroelectrodes (Belding et al., 2010). Here, a conclusion has been made that the voltammetric response from a nanoparticle-modified electrode is substantially different from that expected from a macroelectrode.

The first measurement of comparative electrode kinetics between the nano- and macroscales has been recently reported by Campbell and co-workers. The electrode kinetics and mechanism displayed by the nanoparticle arrays were found to be qualitatively and quantitatively different from those of a silver macrodisk. As was argued by Campbell and co-workers, the electrochemical behaviour of nanoparticles can differ from that of macroelectrodes for a variety of reasons. The most significant among them is that the size of the diffusion layer and the diffuse double layer at the nanoscale can be similar and hence diffusion and migration are strongly coupled. By comparison of the extracted electrode

kinetics the authors stated that for the nanoparticle arrays, the mechanism is likely to be a rate-determining electron transfer followed by a chemical step. As the kinetics displayed by the nanoparticle arrays show changed kinetics from that of a silver macrodisk, they have inferred a change in the mechanism of the rate-determining step for the reduction of 4-nitrophenol in acidic media between the macro- and nanoscales (Campbell et al., 2010). Zhou and co-workers have found the shape and size of voltammograms obtained on silver nanoparticle modified electrodes to be extremely sensitive to the nanoparticle coverage, reflecting the transition from convergent to planar diffusion with increased coverage (Zhou et al., 2010). A system of iron oxide nanoparticles with mixed valencies deposited on photovoltaic amorphous hydrogenated silicon was studied by the kinetic sensitive voltammetry by Gmucová and co-workers. This study was motivated by the previously observed orientation ordering in similar system of nanoparticles involved by a laser irradiation under the applied electric field (Gmucová et al., 2008a). A significant dependence of the kinetic of the redox reactions, in particular oxidation reaction of ferrous ions, was observed as a consequence of the changes in the charged deep states density in amorphous hydrogenated silicon (Gmucová et al., 2008b).

4.2 Carbon nanotubes modified electrodes

Both the preparation and application of carbon nanotubes modified electrodes have been reviewed by Merkoçi, and by Wildgoose and co-workers (Merkoçi, 2006; Wildgoose et al., 2006). The comparative study of electrochemical behaviour of multiwalled carbon nanotubes and carbon black (Obradović et al., 2009) has revealed that although the electrochemical characteristics of properly activated carbon black approaches the characteristics of the carbon nanotubes, carbon nanotubes are superior, especially regarding the electron-transfer properties of the nanotubes with corrugated walls. The kinetics of electron-transfer reactions depends on the morphology of the samples and is faster on the bamboo-like structures, than on the nanotubes with smooth walls. Different oxidation properties of coenzyme NADH on carbon fibre microelectrode and carbon fibre microelectrode modified with branching carbon nanotubes have been reported by Zhao and co-workers (Zhao et al., 2010).

4.3 Thin film or membrane modified electrodes

Thin-layer cells, thin films and membrane systems show theoretical $I-t$ responses that deviate from Cottrell behaviour. Although the diffusion was often assumed to be the only transport mechanism of the electroactive species towards polymer coated electrodes, the migration can contribute significantly. The bulk resistance of film corresponds to a resistance in series with finite diffusional element(s) and leads to ohmic $I-t$ curves at short times. Subsequently, this resistance and the interacting depletion regions give rise to the non-Cottrellian behaviour of thin systems. According to Aoki, when an electrode is coated with a conducting polymer, the Nernst equation in a stochastic process is defined (Aoki, 1991). In such a case the electrode potential is determined by the ratio of the number of conductive (oxidized) species to that of the insulating (reduced) species experienced at the interface which is formed by electric percolation of the conductive domain to the substrate electrode. Examples of evaluating the potential for the case where the film has a random distribution of the conductive and insulating species were presented for three models: a one-dimensional model, a seven-cube model and a cubic lattice model.

Lange and Doblhofer solved the transport equations by digital simulation techniques with boundary conditions appropriate for the system electrode/membrane-type polymer coating (Lange & Doblhofer, 1987). They have concluded that the current transients follow Cottrell equation, however, the observed “effective” diffusion coefficients are different from the tabular ones. In the 90s an important effort has been devoted to examination of the nature of the diffusion processes of membrane-covered Clark-type oxygen sensors by solving the axially symmetric two-dimensional diffusion equation. Gavaghan and co-workers have presented a numerical solution of 2D equations governing the diffusion of oxygen to a circular disc cathode protected from poisoning by the medium to be measured by a tightly stretched plastic membrane which is permeable to oxygen (Gavaghan et al., 1992).

The current-time behaviour of membrane-covered microdisc clinical sensors was examined with the aim to explain their poor performance when pulsed (Sutton et al., 1996). It has been shown by Sutton and co-workers that the Cottrellian hypothesis is not applicable to this type of sensor and it is not possible to predict this behaviour from an analytical expression, as might be the case for membrane-covered macrodisc sensors and unshielded microdisc electrodes.

Gmucová and co-workers have shown that changes in kinetic of a redox reaction manifested as a deviation from the Cottrellian behaviour can be utilized in the preparation of ion selective electrodes. The electroactive hydrophobic end of a molecule used for the Langmuir-Blodgett film modification of a working electrode can induce a change in the kinetic of redox reactions. Ion selective properties of the poly(3-pentylmethoxythiophene) Langmuir-Blodgett film modified carbon-fiber microelectrode have been proved using a model system, mixture of copper and dopamine ions. While in case of the typical steady-state voltammetry the electrode remains sensitive to both the copper and dopamine, the kinetic-sensitive properties of volt coulometry disable the observation of dopamine (Gmucová et al., 2007).

Recently, a sensing protocol based on the anomalous non-Cottrellian diffusion towards nanostructured surfaces was reported by Gmucová and co-workers (Gmucová et al., 2011). The potassium ferrocyanide oxidation on a gold disc electrode covered with a system of partially decoupled iron oxides nanoparticle membranes was investigated using the kinetic-sensitive volt coulometry. Kinetic changes were induced by the altered electrode surface morphology, i.e., micro-sized superparamagnetic nanoparticle membranes were curved and partially damaged under the influence of the applied magnetic field. Thus, the targeted changes in the non-Cottrellian diffusion towards the working electrode surface resulted in a marked amplification of the measured volt coulometric signal. Moreover, the observed effect depends on the membrane elasticity and fragility, which may, according to the authors, give rise to the construction of sensors based on the influence of various physical, chemical or biological external agents on the superparamagnetic nanoparticle membrane Young's moduli.

4.4 Spatially heterogeneous electrodes

Porous electrodes, partially blocked electrodes, microelectrode arrays, electrodes made of composite materials, some modified electrodes and electrodes with adsorbed species are spatially heterogeneous in the electrochemical sense. The simulation of non-Cottrellian electrode responses at such surfaces is challenging both because of the surface variation and

because of the often random distribution of the zones of different electrode activity. The Cottrell equation becomes invalid even if the electrode reaction causes motion of the electrolyte/electrode boundary. Thereby it was modified by Oldham and Raleigh to take account of this effect, as well as to the data published on the inter-diffusion of silver and gold (Oldham & Raleigh, 1971).

Davies and co-workers have shown that by use of the concept of a “diffusion domain” computationally expensive three-dimensional simulations may be reduced to tractable two-dimensional equivalents which gives results in excellent agreement with experiment (Davies et al., 2005). Their approach predicts the voltammetric behaviour of electrochemically heterogeneous electrodes, e.g., composites whose different spatial zones display contrasting electrochemical behaviour toward the same redox couple. Four categories of response on spatially heterogeneous electrode have been defined by the authors depending on the blocked and unblocked electrode surface zones dimensions. In the performed analysis of partially blocked electrodes the difference between “macro” and “micro” was shown to be critical. The question how to specify whether the dimensions of the electro-active or inert zones of heterogeneous electrodes fall into one category or another one can be answered using the Einstein equation, which indicates that the approximate distance, δ , diffused by a species with a diffusion coefficient, D , in a time, t , is $\delta = \sqrt{2Dt}$. The work carried out in the Compton group on methods of fabricating and characterising arrays of nanoelectrodes, including multi-metal nanoparticle arrays for combinatorial electrochemistry, and on numerical simulating and modelling of the electrochemical processes was reviewed in the frontiers article written by Compton (Compton et al., 2008).

An improved sensitivity of voltammetric measurements as a consequence of either electrode or voltammetric cell exposure to low frequency sound was reported by Mikkelsen and Schröder (Mikkelsen & Schröder, 1999; Mikkelsen & Schröder, 2000). According to the authors the longitudinal waves of sound applied during measurements make standing regions with different pressures and densities, which make streaming effects in the boundary layer at least comparable to the conventional stirring. As an alternative explanation of the marked sensitivity enhancement the authors suggested a possible change in the electrical double layer structure. Later, a study of the dopamine redox reactions on the carbon fiber microelectrode by the kinetics-sensitive volt coulometry (Gmucová et al., 2002) revealed an impressive shift towards the ideal kinetic described by Cottrell equation, achieved by an electrochemical pretreatment of the electrode accompanied by its simultaneous exposure to the low frequency sound.

The diffusion equation including the delay of a concentration flux from the formation of a concentration gradient, called diffusion with memory, was formulated by Aoki and solved under chronoamperometric conditions (Aoki, 2006). A slower decay than predicted by the Cottrell equation was obtained.

A theoretical study of the current–time relationship aimed at the explanation of anomalous response in differential pulse polarography was reported by Lovrić and Zelić. The effect was explained by the adsorption of reactant at the electrode surface (Lovrić & Zelić, 2008). The situation connected with the formation of metal preconcentration at the electrode surface, followed by electrodisolution was modelled by Cutters and Compton. The theory to explore the electrochemical signals in such a case at a microelectrode or ultramicroelectrode arrays was derived (Cutress & Compton, 2009).

5. Fractal concepts

A possible cause of the deviation of measured signals from the ideal Cottrellian one is of geometric origin. The irregular (rough, porous or partially active) electrode geometry can and does cause current density inhomogeneities which in turn yield deviations from ideal behaviour. Kinetic processes at non-idealised, irregular surfaces often show non-conventional behaviour, and fractals offer an efficient way to handle irregularity in general terms. Rough and partially active electrodes are frequently modelled using fractal concepts; their surface roughness of limited length scales irregularities is often characterized as self-affine fractal. Fractal geometry is an efficient tool for characterizing irregular surfaces in very general terms. An introduction to the methods of fractal analysis can be found in the work (Le Mehaute & Crepy, 1983). Electrochemistry at fractal interfaces has been reviewed by Pajkossy (Pajkossy, 1991). Diffusion-limited processes on such interfaces show anomalous behavior of the reaction flux.

Pajkossy and co-workers have published an interesting series of papers devoted to the electrochemistry on fractal surfaces (Nyikos & Pajkossy, 1986; Pajkossy & Nyikos, 1989a; Pajkossy & Nyikos, 1989b; Nyikos et al., 1990; Borosy et al., 1991). Diffusion to rough surfaces plays an important role in diverse fields, e.g., in catalysis, enzyme kinetics, fluorescence quenching and spin relaxation. Nyikos and Pajkossy have shown that, as a consequence of fractal electrode surface, the diffusion current is dependent on time as $i \propto t^{-(D_f-1)/2}$, where D_f is the fractal dimension (Nyikos & Pajkossy, 1986). For a smooth, two-dimensional interface ($D_f = 2$) the Cottrell behaviour $i \propto t^{-1/2}$ is obtained. In electrochemical terms this corresponds to a generalized Cottrell equation (or Warburg impedance) and can be used to describe the frequency dispersion caused by surface roughness effects. Later, the verification of the predicted behaviour for fractal surfaces with $D_f > 2$ (rough interface), and $D_f < 2$ (partially blocked surface or active islands on inactive support) was reported (Pajkossy & Nyikos, 1989a). The fractal decay kinetics has been shown to be valid for both contiguous and non-contiguous surfaces, rough or partially active surfaces. Using computer simulation, a mathematical model, and direct experiments on well defined fractal electrodes the fractal decay law has been confirmed for different surfaces. According to the authors, this fractal diffusion model has a feature which deserves some emphasis: this being its generality. It is based on a very general assumption, i.e., self-similarity of the irregular interface, and nothing specific concerning the electrode material, diffusing substance, etc. is assumed. Based on the generalized Cottrell equation, the calculation and experimental verification of linear sweep and cyclic voltammograms on fractal electrodes have been performed (Pajkossy & Nyikos, 1989). The generalized model has been shown to be valid for non-linear potential sweeps as well. Its experimental verification on an electrode with a well defined fractal geometry $D_f = 1.585$ was presented for a rotating disc electrode of fractal surface (Nyikos et al., 1990). The fractal approximation has been shown to be useful for describing the geometrical aspects of diffusion processes at realistic rough or irregular-interfaces (Borosy et al., 1991). The authors have concluded that diffusion towards a self-affine fractal surface with much smaller vertical irregularity than horizontal irregularity leads to the conventional Cottrell relation between current and time of the Euclidean object, not the generalised Cottrell relation including fractal dimension.

The most important conclusions, as outlined in (Pajkossy, 1991), are as follows. If a capacitive electrode is of fractal geometry, then the electrode impedance will be of the constant phase element form (i.e., the impedance, Z , depends on the frequency, ω , as $Z \propto (i\omega)^\beta$ with $0 < \beta < 1$). However, no unique relation between fractal dimension D_f and constant phase element exponent can be established. Assume that a real surface is irregular from the geometrical point of view and that the diffusion-limited current can be measured on it, the surface irregularities can be characterized by a single number, the fractal dimension. The time dependence of the diffusion limited flux to a fractal surface is a power-law function of time, and there is a unique relation ($\beta = (D_f - 1)/2$) between fractal dimension and the exponent β . This equation provides a possibility for the experimental determination of the fractal dimension.

The determination of fractal dimension of a realistic surface has been reported by Ocon and co-workers (Ocon et al., 1991). The thin columnar gold electrodeposits (surface roughness factor 50-100) grown on gold wire cathodes by electroreducing hydrous gold oxide layers have been used for this purpose, the fractal dimension has been determined by measuring the diffusion controlled current of the $\text{Fe}(\text{CN})_4^{4-}/\text{Fe}(\text{CN})_3^{3-}$ reaction. Several examples of diffusion controlled electrochemical reactions on irregular metal electrodeposits type of electrodes were described in (Arvia & Salvarezza, 1994). Using the fractal geometry relevant information about the degree of surface disorder and the surface growth mechanism was obtained and the kinetic of electrochemical reactions at these surfaces was predicted.

Kant has discussed rigorously the anomalous current transient behaviour of self-affine fractal surface in terms of power spectral density of the surface (Kant, 1997). The non-universality and dependence of intermediate time behaviour on the strength of fractality of the interface has been reported, the exact result for the low roughness and the asymptotic results for the intermediate and large roughness of self-affine fractal surfaces have been derived. The intermediate time behaviour of the reaction flux for the small roughness interface has been shown to be proportional to $t^{-1/2} + \text{const } t^{-3/2+H}$, however, for the large roughness interfaces the dependence $\sim t^{-1+H/2}$, where H is Hurst's exponent, was found. For an intermediate roughness a more complicated form has been obtained.

Shin and co-workers investigated the diffusion toward self-affine fractal interfaces by using diffusion-limited current transient combined with morphological analysis of the electrode surface (Shin et al., 2002). Here, the current transients from the electrodes with increasing morphological amplitude (roughness factor) were roughly characterised by the two-stage power dependence before temporal outer cut-off of fractality. Moreover, the authors suggested a method to interpret the anomalous current transient from the self-affine fractal electrodes with various amplitudes. This method, describing the anomalous current transient behaviour of self-affine electrodes, includes the determination of the apparent self-similar scaling properties of the self-affine fractal structure by the triangulation method.

A general transport phenomenon in the intercalation electrode with a fractal surface under the constraint of diffusion mixed with interfacial charge transfer has been modelled by using the kinetic Monte Carlo method based upon random walk approach (Lee & Pyun, 2005). Go and Pyun (Go & Pyun, 2007) reviewed anomalous diffusion towards and from fractal interface. They have explained both the diffusion-controlled and non-diffusion-controlled transfer processes. For the diffusion coupled with facile charge-transfer reaction the

electrochemical responses at fractal interface were treated with the help of the analytical solutions to the generalised diffusion equation. In order to provide a guideline in analysing anomalous diffusion coupled with sluggish charge-transfer reaction at fractal interface, i.e., non-diffusion-controlled transfer process across fractal interface, this review covered the recent results concerned to the effect of surface roughness on non-diffusion-controlled transfer process within the intercalation electrodes. It has been shown, that the numerical analysis of diffusion towards and from fractal interface can be used as a powerful tool to elucidate the transport phenomena of mass (ion for electrolyte and atom for intercalation electrode) across fractal interface whatever controls the overall transfer process.

A theoretical method based on limited scale power law form of the interfacial roughness power spectrum and the solution of diffusion equation under the diffusion-limited boundary conditions on rough interfaces was developed by Kant and Jha (Kant & Jha, 2007). The results were compared with experimentally obtained currents for nano- and micro-scales of roughness and are applicable for all time scales and roughness factors. Moreover, this work unravels the connection between the anomalous intermediate power law regime exponent and the morphological parameters of limited scales of fractality.

Kinetic response of surfaces defined by finite fractals has been addressed in the context of interaction of finite time independent fractals with a time-dependent diffusion field by a novel approach of Cantor Transform that provides simple closed form solutions and smooth transitions to asymptotic limits (Nair & Alam, 2010). In order to enable automatic simulation of electrochemical transient experiments performed under conditions of anomalous diffusion in the framework of the formalism of integral equations, the adaptive Huber method has been extended onto integral transformation kernel representing fractional diffusion (Bieniasz, 2011).

The fractal dimension can be simply estimated using the kinetics-sensitive volt coulometry introduced by Thurzo and co-workers (Thurzo et al., 1999). On the basis of the multipoint analysis principles the transient charge is sampled at three different events in the interval between subsequent excitation pulses and the sampled values are combined according the appropriate filtering scheme. The third sampling event chosen at the end of measuring period and slow potential scans make the observation of non-Cottrellian responses easier. The parameter β that enters the power-law time dependence of the transient charge, as well as the fractal dimension can be simply determined from two volt coulograms obtained for two distinct sets of sampling events (Gmucová et al., 2002).

6. Conclusion

The electrode surface attributes have a profound influence on the kinetic of electron transfer. The continued progress in material research has induced the marked progress in the preparation of electrochemical electrodes with enhanced sensitivity or selectivity. If such a sophisticated electrode with microstructured, nanostructured or electroactive surface is used a special attention should be paid to a careful examination of changes initiated in the diffusion towards its surface. Newly designed types of electrochemical electrodes often result in more or less marked deviations from the ideal Cottrell behaviour. Various modifications of the relationship (Equation (1)) have been investigated to describe the processes in real electrochemical cells. A raising awareness of the importance of a detailed

knowledge on the kinetic of charge transfer during the studied redox reaction has lead to a significant number of theoretical, computational, phenomenological and, last but not least, experimental studies. Based on them one can conclude: nowadays, an un-usual behaviour is the Cottrellian one.

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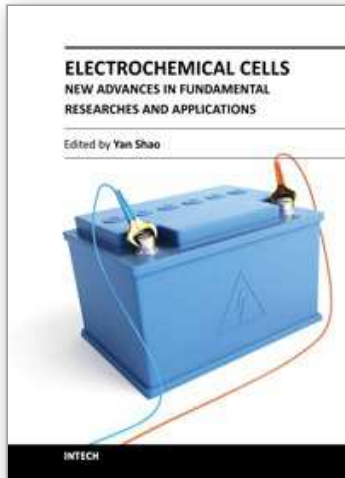
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