



Mini review

Recent advances on the theory of pulse techniques: A mini review



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ABSTRACT

The theory recently developed for the main double- and multi- potential pulse techniques is reviewed, enabling us to benefit from using such techniques in mechanistic and kinetic quantitative studies. First, easy-to-implement analytical and semi-analytical solutions are considered for many common electrochemical problems. For more complex experimental situations, efficient numerical methods are available as well as software packages.

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Contents

1.	Introduction	25
2.	Double potential pulse techniques	26
2.1.	Double pulse chronoamperometry (DPC)	26
2.2.	Reverse pulse voltammetry (RPV).	26
2.3.	Differential double pulse voltammetry (DDPV) and additive differential double pulse voltammetry (ADDPV)	26
3.	Multipulse techniques.	27
3.1.	Differential multi pulse voltammetry (DMPV)	27
3.1.1.	Analytical solutions	27
3.1.2.	Semi-analytical solutions.	27
3.2.	Staircase voltammetry (SCV) and differential staircase voltammetry (DSCV)	27
3.2.1.	Analytical solutions	28
3.2.2.	Semi-analytical solutions.	28
3.3.	Square wave voltammetry (SWV)	28
3.3.1.	Solution-phase systems	28
3.3.2.	Surface-bound systems	28
3.3.3.	Liquid/liquid interfaces.	28
4.	Numerical simulation of pulse techniques	28
4.1.	Finite-difference methods.	28
4.2.	Finite-element methods	29
	Disclosure statement.	29
	Conflict of interest	29
	Acknowledgments	29
	References	29

1. Introduction

This review aims to highlight the most recent contributions to the application of potential pulse techniques beyond electroanalytical purposes. These methods offer a number of advantages for quantitative

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studies, mainly well-defined and peak-shaped responses where undesirable effects are greatly minimized. Therefore, these techniques are very valuable in mechanistic and kinetic quantitative studies making use of the broad theoretical framework available.

The common feature of the voltammetric techniques considered in this review is that the applied potential difference remains constant over a period of time (so-called *potential pulse*) and afterwards the potential difference is set to a different constant value, either in the potential region of the faradaic process under study or outside this region to recover the initial equilibrium conditions (see Figs. 1 and 2). The current response is recorded at the end of the potential pulses so the effects associated with the double layer charging are greatly reduced. Based on this, a variety of electrochemical techniques have been designed with different voltammetric waveforms and treatments of the system response. Attending to the perturbation, the number of potential pulses applied before recovering the equilibrium conditions is a commonly-employed classification criterion. Thus, in *single-*, *double-* and *triple-* pulse techniques the equilibrium is regained after one, two and three consecutive potential pulses, respectively, whereas in *multipulse* techniques equilibrium conditions are only retrieved at the end of the experiment.

Double- and multi- pulse techniques are the most widely employed and this review is devoted to them, including conventional and recently-developed methods. In the first part, special attention will be paid to simple diagnosis criteria, experimental methodologies and easy-to-implement solutions for kinetic, mechanistic and mass transport studies. This will include analytical solutions, from which the electrochemical behaviour of the system can be analyzed *a priori*, as well as semi-analytical solutions that also allow the system to be simulated without special computational skills. Lastly, the use of numerical methods will be considered for situations complicated by the (electro) chemical kinetics, the electrode geometry, the heterogeneity of the electrode surface or the resistivity of the medium.

2. Double potential pulse techniques

2.1. Double pulse chronoamperometry (DPC)

Under appropriate conditions DCP is very valuable for the simultaneous study of the diffusivity and reactivity of both the reactant and product electroactive species, especially when the product is not stable in the working solution. For simplicity, it is convenient to avoid the influence of the electrode kinetics so the first potential pulse is usually set at values corresponding to limiting current conditions for the

reactant and the second pulse to limiting current conditions of the electrogenerated product. Under these conditions, a rigorous analytical solution has been deduced for electron transfer processes without chemical complications at (hemi)spherical electrodes of any size [1]. This solution has clearly shown that, in the most interesting situation where only the reactant species is initially present in the electrolyte solution, the response in DPC is not sensitive to the diffusion coefficient of the product at macroelectrodes, whereas at ultramicroelectrodes the current in the second pulse is too small. From both behaviours, the optimum conditions for the simultaneous determination of the diffusion coefficients have been established in the range $2.0 > r_0 / \sqrt{D_A} \tau_1 > 0.8$ [2], where D_A is the diffusion coefficient of the reactant species.

DPC with limiting current potentials is also suitable for studying coupled homogeneous chemical reactions where the product species participates. A simple analytical solution has been obtained for the (pseudo)first-order EC mechanism in DPC at (hemi)spherical electrodes of any size that yields accurate results when the chemical process is fast enough [3].

2.2. Reverse pulse voltammetry (RPV)

In RPV a series of double potential pulses are applied where the product is always generated in the first under diffusion-controlled conditions, the potential of the second is set at different values (E_2) and the current recorded at the end of this pulse (I_2) (see Fig. 1). Thus, the thermodynamics and kinetics of the electron transfer can be studied from the position and shape of the RPVgram: I_2 vs E_2 . A rigorous analytical solution is available for simple electron transfer processes at spherical electrodes of any radius and for any reversibility degree [4]. For homogeneous follow-up reactions, a solution for the (pseudo)first-order $E_{rev}C$ mechanism in RPV at (hemi)spherical electrodes has been deduced for the quantification of fast chemical kinetics [3]. RPV in combination with microelectrodes is reported to be useful in the study of processes where the product is “assimilated” by the electrode, like amalgamation at mercury droplets [5]. Thus, the appearance of an atypical peak in the RPVgram as a consequence of the depletion of the species inside the electrode provides a simple diagnostic criterion.

2.3. Differential double pulse voltammetry (DDPV) and additive differential double pulse voltammetry (ADDPV)

In DDPV the duration of the second pulse is much shorter than the first ($\tau_1/\tau_2 = 50 - 100$) and the potential values of *both* pulses are varied within the potential region of interest, the difference between them

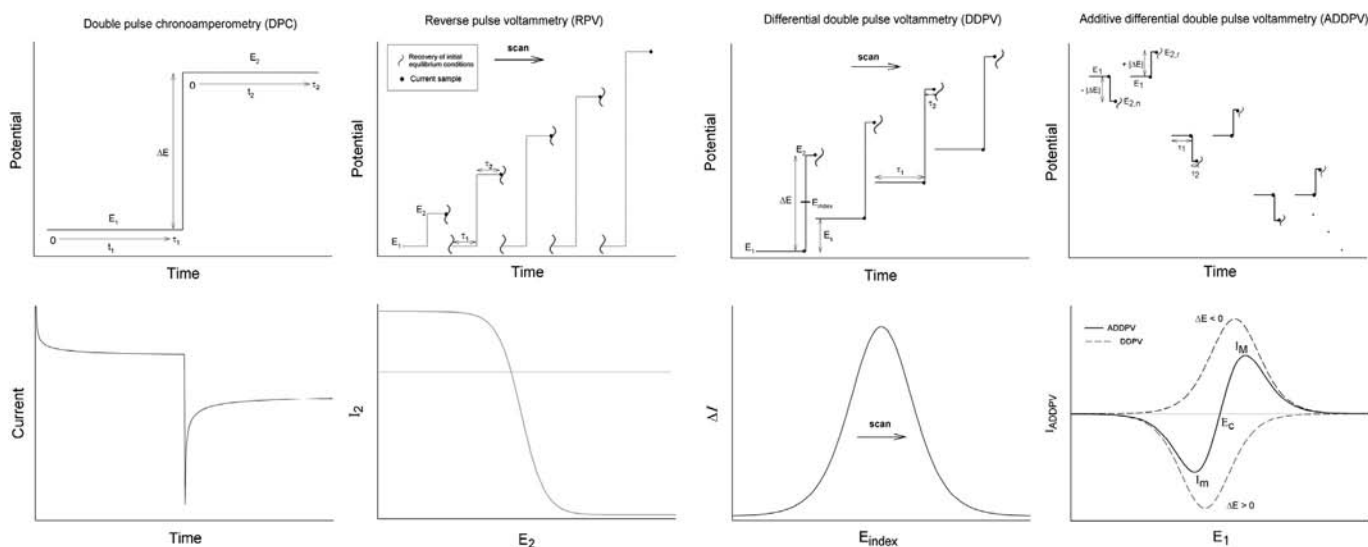


Fig. 1. Perturbation (upper graphs) and signal (lower graphs) of the double pulse techniques considered in this review.

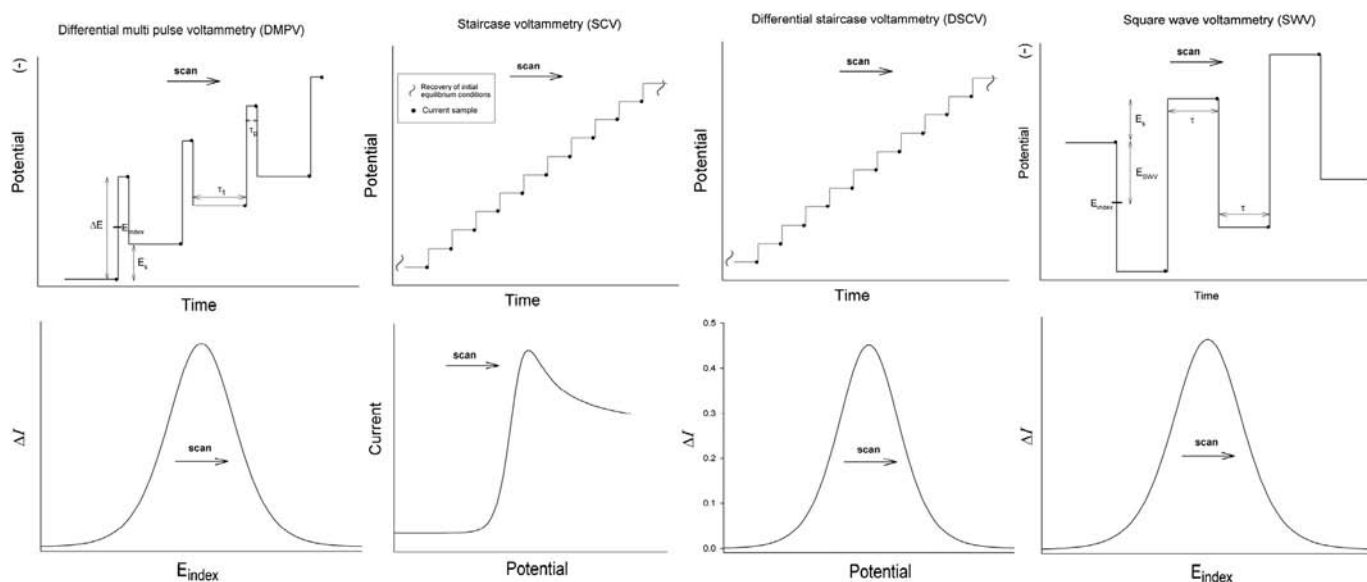


Fig. 2. Perturbation (upper graphs) and signal (lower graphs) of the multipulse techniques considered in this review.

(pulse amplitude, $\Delta E = E_2 - E_1$) remains constant along the experiment (Fig. 1). The DPVgram corresponds to the plot $\Delta I = I_2 - I_1$ versus a potential-axis. Traditionally, the E_1 -value has been chosen as the potential-axis, though our group recently proposed using the arithmetic average: $E_{1,2} = (E_2 + E_1)/2$ [6].

ADDPV is an extension of DDPV where two DDPV experiments are performed with the same technique parameters but different pulse amplitude signs. The resulting ΔI vs E_1 curves for $\Delta E > 0$ and $\Delta E < 0$ are summed and as a result, the characteristic ADDPV signal is obtained that shows a maximum, a minimum and a null current potential, E_c (Fig. 1). The latter is the most interesting feature of this method since it can be measured more accurately than peak or half-wave potentials.

Simple analytical equations for DDPV and ADDPV with macroelectrodes and spherical microelectrodes have been obtained for the determination of diffusion coefficients and formal potential of reversible one-electron processes [6], determination of the formal potentials of reversible multi-electron transfers [7,8], electrode kinetic studies [9,10], identification and characterization of coupled chemical reactions (including (pseudo)first-order catalytic, CE and EC mechanisms [11,12]) and amalgamation processes [5]. DDPV has also been applied in the study of reversible ion transfers through liquid/liquid interfaces [13].

3. Multipulse techniques

In multipulse techniques a series of potential pulses are applied and the initial equilibrium conditions of the system are regained only at the end of the experiment. This enables us to decrease the experimental time but makes the theoretical treatment more complex. In spite of this, analytical solutions have been derived recently for some common mechanisms and electrode geometries, including non-uniformly accessible electrodes, like microdiscs, that had been addressed so far by means of numerical methods (Section 4). An “intermediate” approach is employed by Lovrić’s, Mirceski’s and Gulaboski’s groups where the integral solutions resulting from Laplace transforms are evaluated numerically, mainly making use of the standard step-function method. The electrochemical response is obtained as a system of recursive formulae that will be referred hereon to as *semi-analytical solutions*, which are easier to implement than “pure” numerical methods though they do not enable *a priori* analysis of the system as analytical solutions do.

It is worth mentioning the lack of universal and unambiguous names for the different pulse techniques. The recovery of equilibrium

conditions at stationary electrodes can be time-consuming, especially in the case of macroelectrodes. Therefore, multipulse “versions” of existing (single- and) double-pulse polarographic techniques were designed. Nevertheless, the same term has been often employed to refer to both the double pulse and the multipulse “modes”. Whereas the latter are the most frequently available in commercial potentiostats,¹ the modelling of the former is easier. As discussed in a recent paper [14], this situation can lead to inappropriate data analysis since only in the DMPV of reversible processes when $\tau_p < \tau_1$ or when microelectrodes are employed (steady state voltammetry) do the responses in double pulse and multipulse techniques coincide. To distinguish clearly between them, here we use the nomenclature proposed in [14].

3.1. Differential multi pulse voltammetry (DMPV)

As mentioned, DMPV can be viewed as the multiple “version” of DDPV and it is by far the most frequent in commercial potentiostats referred to as differential pulse voltammetry.

3.1.1. Analytical solutions

The analytical expressions deduced for single and multiple reversible electron transfers in [15] and for the (pseudo)first-order $E_{rev}C'$ mechanism in [16] at planar, spherical and disc electrodes can be particularized easily for the potential-time perturbation applied in DMPV.

3.1.2. Semi-analytical solutions

The effects associated to the electrode kinetics and the adsorption of the reactant species on the DMPVgram of one-electron transfers at planar electrodes can be considered from the recursive formulae reported in [17].

3.2. Staircase voltammetry (SCV) and differential staircase voltammetry (DSCV)

True linear sweep or cyclic voltammeteries cannot be applied in modern digital potentiostats, the real perturbation corresponding to SCV (see Fig. 1) with small potential steps. DSCV is an interesting variant of SCV that makes the determination of formal potentials more accurate.

¹ The implementation of single- and double-pulse techniques (as well as any other potential-time perturbations) by the user is possible and increasingly more easily in modern potentiostats.

3.2.1. Analytical solutions

Analytical expressions for both SCV and SCV at planar, spherical and disc electrodes have been deduced for single and multiple reversible electron transfers [15,18] and for the (pseudo)first-order $E_{rev}C'$ mechanism [16].

Electroactive monolayers have also been considered and an analytical solution for the study of two-electron processes has been reported as a recursive expression [19]. Solutions for the quantification of the electrocatalytic activity of electroactive monolayers by (pseudo)first-order and second-order catalytic reactions are given in [20] and [21], respectively.

3.2.2. Semi-analytical solutions

Different two-electron transfer mechanisms of surface-bound electroactive species were studied by Gulaboski *et al.* [22] in staircase voltammetry. These include the EE, (pseudo)first-order ECE and (pseudo)first-order EEC' mechanisms.

3.3. Square wave voltammetry (SWV)

SWV is the most popular pulse technique and widely considered for mechanistic and kinetic studies as complementary to cyclic voltammetry. The theory of common solution-phase and surface-bound redox systems at planar and (hemi)spherical electrodes is well established and can be found in [23–26].

3.3.1. Solution-phase systems

3.3.1.1. Analytical solutions. For multiple electron transfers, analytical solutions for the SWV curves have been deduced [27,28] for any electrode geometry (including planar, disc and (hemi)spherical electrodes) when the electrochemical steps are reversible; these allow accurate determination of formal potentials and therefore of the thermodynamic stability of the electroactive species. Solutions for the (pseudo)first-order $E_{rev}C'$ mechanism have also been reported [29].

3.3.1.2. Semi-analytical solutions. A new strategy for the study of the electrode kinetics of one-electron processes at planar and (hemi)spherical electrodes at a constant scan rate has been developed by Mirceski *et al.* [30,31]. This approach is based on the analysis of the variation of the peak potential and current of the SWV curves with the pulse amplitude. The use of the half-peak width has also been explored in [32].

A solution for two-electron processes at planar electrodes is available and has been applied to SWV in direct and reverse scan modes [33]. The latter is a modification of conventional SWV experiments where the scan starts at potentials where the electrode reaction is controlled by mass transport.

Mechanisms where the electron transfer reaction at planar electrodes is complicated by coupled chemical reactions have also been addressed following the semi-analytical approach mentioned above: the $EC_{eq}E$ mechanism where the chemical reaction is always at equilibrium [34], electron transfers followed by the dimerization of the product [35] and the (pseudo)first-order catalytic mechanism of the second kind [36].

3.3.2. Surface-bound systems

3.3.2.1. Analytical solutions. Solutions for the study of the (pseudo)first-order [20] and second-order [37] electrocatalysis by a redox couple immobilized at (hemi)spherical microelectrodes have been obtained.

Molina's group has proposed two new multipotential pulse techniques for the study of electroactive monolayers called square wave voltacoulometry (SWVC) [38–41] and differential staircase voltacoulometry (DSVC) [42], based on the analysis of the difference of converted charge signals obtained between two successive half-cycles. These techniques were applied to the study of quasi-reversible and reversible one-electron processes [38,40], (pseudo)first order electrocatalysis with the catalyst confined at the electrode surface [38, 39] and two-electron reversible processes [41,42].

3.3.2.2. Semi-analytical solutions. The constant scan rate [30,31] and half-peak width [32] strategies have also been applied to the study of the electron transfer kinetics of surface-bound redox systems. Solutions for the (pseudo)first-order ECE [43] and EEC' [44] mechanisms as well as for different stripping processes at planar electrodes [45,46] are also available.

3.3.3. Liquid/liquid interfaces

In recent years the theory for electron transfers at electrode/electrolyte interfaces has been extended to the study of simple [47–53] and facilitated [48,54] ion transfer at liquid/liquid interfaces.

4. Numerical simulation of pulse techniques

Sophisticated numerical methods developed over years [55–58] provide a more general approach to electrochemical problems with regard to reaction mechanisms and electrode geometries. The implementation of homemade numerical simulations requires some knowledge of computer programming. Alternatively, some ready-to-use software packages include the simulation of pulse techniques (Table 1).

4.1. Finite-difference methods

In recent years some significant contributions have been made in the optimization of finite-difference methods for the simulation of pulse techniques where computation time can be problematic and hardware-demanding due to the use of very short time-steps to follow rapid changes in concentrations just after the potential jumps. A simple method that combines highly expanding grids with asymmetric 4-point approximation of the spatial derivatives and fourth-order extrapolation scheme for time integration is very efficient for the E mechanism in pulse voltammetries at planar and (hemi)spherical electrodes [59]. For electron transfer processes complicated by chemical reactions and for single- and multi-pulse chronoamperometries, the Crank–Nicholson algorithm preceded by four second-order extrapolation steps is more convenient [60]. Britz *et al.* [61] recently examined the simulation of diffusion-limited chronoamperometry at disc microelectrodes with a wide range of approaches finding as the most efficient the use of a spatial grid transformed according to the Verbrugge–Baker conformal map

Table 1
Software packages that include the simulation of pulse techniques.

Package	Techniques	Electrode geometries	Supplier
DIGIELCH	CV, chronoamperometry, SWV, Fourier transform voltammetry, EIS	Planar, spherical, band, disc thin layer cells	www.gamry.com/products/digielch-electrochemical-simulation-software
ELECTROCHEMIST (former POLAR)	CV, NPV, DDPV, RPV, SWV, chronoamperometry	Planar, spherical, band, disc, ring thin layer cells	www.electrochemist.com
KISSA	CV, LSV, chronoamperometry	Planar, spherical, cylindrical, disc, band	More information in: www.kissagroup.com/
ELECTROVISION	CV, NPV, DDPV, RPV, SWV, chronoamperometry	Planar, spherical, cylindrical	Available under request in: www.um.es/electroquimica
ECHEM++	CV, EIS, chronoamperometry,	Planar, spherical, cylindrical	www.echem.uni-tuebingen.de/echem/software/ECHEM++/echem++_shtml

together with a time marching method. Other strategies employed to reduce the simulation time of chronoamperometric experiments include expanding [62–64] and adaptive [65] time grids.

The application of potential pulse techniques to “awkward” electrochemical systems has been developed making use of finite-difference methods, such as experiments in highly resistive media [66–68], electron transfers at hydrodynamic electrodes [69] and electrodes modified by porous layers [70], ohmic drop, double layer effects and complex electrochemical mechanisms [71], metal electrodeposition [72,73] and generator-collector mode experiments [74]. Assisted by finite-difference methods, DDPV and SWV have also been employed in the assessment of electron transfer kinetic models [75,76] and modifications of conventional techniques have been proposed. Thus, Jadresko and Zelic have designed several multipulse voltammetries (so-called cyclic multi pulse, cyclic differential multi pulse and cyclic square wave voltammetries) and investigated their application to the study of electrode kinetics [77] and the (pseudo)first-order $E_{rev}C$ mechanism [78].

4.2. Finite-element methods

Finite-element methods (FEM) provide more flexibility to address electrochemical problems, though the mathematical complexity is higher [79]. Nevertheless, complex electrode geometries are increasingly common and free and commercial software packages exist that greatly facilitate the use of FEMs [80]. Regarding commercial packages, for a very recent review on the use of COMSOL Multiphysics® for electrochemical analysis see [81].

Disclosure statement

None.

Conflict of interest

None.

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References

- [1] Á. Molina, C. Serna, F. Martínez-Ortiz, E. Laborda, *Electrochem. Commun.* 10 (2008) 376.
- [2] Á. Molina, R.G. Compton, C. Serna, F. Martínez-Ortiz, E. Laborda, *Electrochim. Acta* 54 (2009) 2320.
- [3] A. Molina, E. Laborda, F. Martínez-Ortiz, E. Torralba, R.G. Compton, *Electrochim. Acta* 87 (2013) 416.
- [4] Á. Molina, F. Martínez-Ortiz, E. Laborda, R.G. Compton, *J. Electroanal. Chem.* 648 (2010) 67.
- [5] F. Martínez-Ortiz, E. Laborda, J.G. Limon-Petersen, E.I. Rogers, C. Serna, N.V. Rees, A. Molina, R.G. Compton, *J. Phys. Chem. C* 113 (2009) 17215.
- [6] Á. Molina, E. Laborda, E.I. Rogers, F. Martínez-Ortiz, C. Serna, J.G. Limon-Petersen, N.V. Rees, R.G. Compton, *J. Electroanal. Chem.* 634 (2009) 73.
- [7] Á. Molina, J. González, E. Laborda, R.G. Compton, *Int. J. Electrochem. Sci.* 7 (2012) 5765.
- [8] A. Molina, J. Gonzalez, E. Laborda, Q. Li, C. Batchelor-McAuley, R.G. Compton, *J. Phys. Chem. C* 116 (2012) 1070.
- [9] Á. Molina, F. Martínez-Ortiz, E. Laborda, R.G. Compton, *Electrochim. Acta* 55 (2010) 5163.
- [10] E. Laborda, E.I. Rogers, F. Martínez-Ortiz, Á. Molina, R.G. Compton, *Electroanalysis* 22 (2010) 2784.
- [11] E. Laborda, F. Martínez-Ortiz, Á. Molina, *Electrochim. Acta* 56 (2011) 5335.
- [12] E. Laborda, F. Martínez-Ortiz, Á. Molina, *Electroanalysis* 22 (2010) 1857.
- [13] A. Molina, C. Serna, J.A. Ortuño, J. González, E. Torralba, A. Gil, *Anal. Chem.* 81 (2009) 4220.
- [14] A. Molina, E. Laborda, F. Martínez-Ortiz, D.F. Bradley, D.J. Schiffrin, R.G. Compton, *J. Electroanal. Chem.* 659 (2011) 12.
- [15] A. Molina, C. Serna, Q. Li, E. Laborda, C. Batchelor-McAuley, R.G. Compton, *J. Phys. Chem. C* 116 (2012) 11470.
- [16] A. Molina, J. González, E. Laborda, Y. Wang, R.G. Compton, *Phys. Chem. Chem. Phys.* 13 (2011) 14694.
- [17] M. Zelič, M. Lovrić, *Electroanalysis* 23 (2011) 642.
- [18] M. López-Tenés, C. Serna, M.M. Moreno, Á. Molina, *Port. Electrochim. Acta* 25 (2007) 103.
- [19] J. Gonzalez, M. Lopez-Tenes, A. Molina, *J. Phys. Chem. C* 117 (2013) 5208.
- [20] J. González, C.M. Soto, Á. Molina, *Electrochim. Acta* 54 (2009) 6154.
- [21] A. Molina, J. González, E. Laborda, F. Martínez-Ortiz, L.K. Bieniasz, *J. Phys. Chem. C* 114 (2010) 14542.
- [22] R. Gulaboski, P. Kokoškarova, S. Mitrev, *Electrochim. Acta* 69 (2012) 86.
- [23] R. Gulaboski, V. Mirčeski, I. Bogeski, M. Hoth, *J. Solid State Electrochem.* 16 (2012) 2315.
- [24] V. Mirčeski, R. Gulaboski, M. Lovrić, I. Bogeski, R. Kappl, M. Hoth, *Electroanalysis* 25 (2013) 2411.
- [25] V. Mirčeski, S. Komorsky-Lovrić, M. Lovrić, *Square-Wave Voltammetry Theory and Application*, Springer, Berlin; London, 2007.
- [26] A. Molina, J. Gonzalez, E. Laborda, R.G. Compton, *Russ. J. Electrochem.* 48 (2012) 600.
- [27] E. Laborda, A. Molina, Q. Li, C. Batchelor-McAuley, R.G. Compton, *Phys. Chem. Chem. Phys.* 14 (2012) 8319.
- [28] A. Molina, M.M. Moreno, C. Serna, M. López-Tenés, J. González, N. Abenza, *J. Phys. Chem. C* 111 (2007) 12446.
- [29] A. Molina, J. González, E. Laborda, Y. Wang, R.G. Compton, *Phys. Chem. Chem. Phys.* 13 (2011) 16748.
- [30] V. Mirčeski, D. Guziejewski, K. Lisichkov, *Electrochim. Acta* 114 (2013) 667.
- [31] V. Mirčeski, E. Laborda, D. Guziejewski, R.G. Compton, *Anal. Chem.* 85 (2013) 5586.
- [32] R. Gulaboski, M. Lovrić, V. Mirčeski, I. Bogeski, M. Hoth, *Biophys. Chem.* 138 (2008) 130.
- [33] S. Komorsky-Lovrić, M. Lovrić, *Int. J. Electrochem. Sci.* 9 (2014) 435.
- [34] S. Komorsky-Lovrić, M. Lovrić, *Anal. Bioanal. Electrochem.* 5 (2013) 291.
- [35] M. Lovrić, D. Jadreško, S. Komorsky-Lovrić, *Electrochim. Acta* 90 (2013) 226.
- [36] V. Mirčeski, A. Bobrowski, J. Zarebski, F. Spasovski, *Electrochim. Acta* 55 (2010) 8696.
- [37] J. Gonzalez, A. Molina, F. Martinez Ortiz, E. Laborda, *J. Phys. Chem. C* 116 (2012) 11206.
- [38] J. Gonzalez, A. Molina, *J. Solid State Electrochem.* 17 (2013) 537.
- [39] J. González, C.M. Soto, A. Molina, *J. Electroanal. Chem.* 634 (2009) 90.
- [40] J. González, A. Molina, N. Abenza, C. Serna, M.M. Moreno, *Anal. Chem.* 79 (2007) 7580.
- [41] J. Gonzalez, A. Molina, M. Lopez-Tenes, F. Karimian, *Anal. Chem.* 85 (2013) 8764.
- [42] J. González, A. Molina, C.M. Soto, C. Serna, *J. Electroanal. Chem.* 664 (2012) 53.
- [43] R. Gulaboski, *J. Solid State Electrochem.* 13 (2009) 1015.
- [44] R. Gulaboski, L. Mihajlov, *Biophys. Chem.* 155 (2011) 1.
- [45] V. Mirčeski, D. Guziejewski, W. Ciesielski, *Electroanalysis* 23 (2011) 1365.
- [46] V. Mirčeski, S.B. Hocevar, B. Ogorevc, R. Gulaboski, I. Drangov, *Anal. Chem.* 84 (2012) 4429.
- [47] R. Gulaboski, V. Mirceski, C.M. Pereira, M.N.D. Cordeiro, A.F. Silva, F. Quentel, M. L'Her, M. Lovric, *Langmuir* 22 (2006) 3404.
- [48] R. Gulaboski, C.M. Pereira, M.N.D. Cordeiro, I. Bogeski, E. Ferreira, D. Ribeiro, M. Chirea, A.F. Silva, *J. Phys. Chem. B* 109 (2005) 12549.
- [49] Á. Molina, J.A. Ortuño, C. Serna, E. Torralba, *Phys. Chem. Chem. Phys.* 12 (2010) 13296.
- [50] A. Molina, J.A. Ortuño, C. Serna, E. Torralba, J. González, *Electroanalysis* 22 (2010) 1634.
- [51] A. Molina, C. Serna, J. González, J.A. Ortuño, E. Torralba, *Phys. Chem. Chem. Phys.* 11 (2009) 1159.
- [52] J.A. Ortuno, C. Serna, A. Molina, E. Torralba, *Electroanalysis* 21 (2009) 2297.
- [53] F. Quentel, V. Mirceski, C. Elleouet, M. L'Her, *J. Phys. Chem. C* 112 (2008) 15553.
- [54] A. Molina, E. Torralba, C. Serna, J.A. Ortuño, *Electrochim. Acta* 106 (2013) 244.
- [55] L.K. Bieniasz, D. Britz, *Pol. J. Chem.* 78 (2004) 1195.
- [56] D. Britz, *Digital Simulation in Electrochemistry*, Springer, 2005.
- [57] R.G. Compton, E. Laborda, K.R. Ward, *Understanding Voltammetry: Simulation of Electrode Processes*, 2013.
- [58] K. Ludwig, L. Rajendran, B. Speiser, *J. Electroanal. Chem.* 568 (2004) 203.
- [59] F. Martínez-Ortiz, N. Zoroa, Á. Molina, C. Serna, E. Laborda, *Electrochim. Acta* 54 (2009) 1042.
- [60] F. Martínez-Ortiz, A. Molina, E. Laborda, *Electrochim. Acta* 56 (2011) 5707.
- [61] D. Britz, O. Østerby, J. Strutwolf, *Electrochim. Acta* 78 (2012) 365.
- [62] E.O. Barnes, L. Xiong, K.R. Ward, R.G. Compton, *J. Electroanal. Chem.* 701 (2013) 59.
- [63] O.V. Klymenko, R.G. Evans, C. Hardacre, I.B. Svir, R.G. Compton, *J. Electroanal. Chem.* 571 (2004) 211.
- [64] C. Amatore, I. Svir, *J. Electroanal. Chem.* 557 (2003) 75.
- [65] L.K. Bieniasz, *J. Electroanal. Chem.* 565 (2004) 273.
- [66] Y. Wang, E.O. Barnes, E. Laborda, A. Molina, R.G. Compton, *J. Electroanal. Chem.* 673 (2012) 13.
- [67] D. Krulic, N. Fatouros, *J. Electroanal. Chem.* 652 (2011) 26.
- [68] D. Krulic, N. Fatouros, *J. Electroanal. Chem.* 655 (2011) 116.
- [69] A.B. Miles, R.G. Compton, *J. Electroanal. Chem.* 499 (2001) 1.
- [70] E. Laborda, A. Molina, F. Martínez-Ortiz, R.G. Compton, *Electrochim. Acta* 73 (2012) 3.
- [71] M. Rudolph, *J. Electroanal. Chem.* 503 (2001) 15.
- [72] N. Fatouros, D. Krulic, H. Groult, *J. Electroanal. Chem.* 625 (2009) 1.

- [73] N. Fatouros, D. Krulic, J. Electroanal. Chem. 706 (2013) 76.
- [74] G.E. Lewis, S.E. Dale, B. Kasprzyk-Hordern, E.O. Barnes, R.G. Compton, F. Marken, *Electroanalysis* 24 (2012) 1726.
- [75] E. Laborda, M.C. Henstridge, A. Molina, F. Martínez-Ortiz, R.G. Compton, J. Electroanal. Chem. 660 (2011) 169.
- [76] M.C. Henstridge, E. Laborda, Y. Wang, D. Suwatchara, N. Rees, Á. Molina, F. Martínez-Ortiz, R.G. Compton, J. Electroanal. Chem. 672 (2012) 45.
- [77] D. Jadresko, M. Zelić, J. Electroanal. Chem. 707 (2013) 20.
- [78] D. Jadresko, M. Zelić, J. Electroanal. Chem. 714 (2014) 30.
- [79] D.J. Gavaghan, K. Gillow, E. Süli, *Langmuir* 22 (2006) 10666.
- [80] http://en.wikipedia.org/wiki/List_of_finite_element_software_packages.
- [81] E.J.F. Dickinson, H. Ekström, E. Fontes, *Electrochem. Commun.* 40 (2014) 71