Mini review

COMSOL Multiphysics®: Finite element software for electrochemical analysis. A mini-review

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ABSTRACT

We discuss the use of the commercial finite element software COMSOL Multiphysics® for electrochemical analysis. Practical considerations relevant to finite element modelling are highlighted. A review of contemporary applications of this software is supplied; the subjects concerned reveal the particular suitability of general-purpose finite element methods for non-standard geometries, complex reaction chemistry, hydrodynamic electrochemistry, and rapid verification of standard results.

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Contents

1. Introduction

COMSOL Multiphysics® (known as FEMLAB before 2005) is a commercial finite element software package designed to address a wide range of physical phenomena [1]. Noting the increased use of this product in analytical electrochemistry, the authors aim to review its relevance and practical use in this field. Accordingly we shall discuss briefly the fundamentals of electrochemical simulation and the methods implemented by COMSOL Multiphysics to address these.

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2. Electrochemical theory

A short review does not allow a comprehensive exposition of electrochemical theory, but we shall discuss the most important standard assumptions. Electrochemical phenomena are governed by the coupling of the conservation of charge and current in the electrolyte and electrodes, together with the conservation of mass for each solute species in an electrolyte. Prediction of a fluid flow additionally involves the conservation of momentum and total mass in a solution or mixture.

These phenomena are normally described mathematically using partial differential equations (PDEs). Therefore, electrochemical theory is developed by solving such PDEs on a suitable geometry and timescale.

Except for simple cases, these equations lack exact mathematical solutions, and so computational solution is required.

In the most general case, charge conservation obeys Gauss's law (Eq. (1)), and mass transport obeys the Nernst–Planck equations (Eq. (2), for an ideal solution) subject to mass continuity (Eq. (3)):

$$-\nabla \cdot (\varepsilon \nabla \varphi) = \rho \tag{1}$$

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_i c_i \nabla \varphi + c_i \mathbf{u} \tag{2}$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_i \tag{3}$$

ε − permittivity (F m^{-1}); φ − potential (V); ρ − charge density (C m^{-3}); c_i − concentration of species i (mol m^{-3}); $\mathbf{N}_i$ − flux of species i (mol m^{-2} s^{-1}); D_i − diffusion coefficient of species i (m^2 s^{-1}); z_i − charge number of species i; u_i − mobility of species i (m^2 V^{-1} s^{-1}); $\mathbf{u}$ − bulk velocity (m s^{-1}); R_i − mass source of species i (mol m^{-3} s^{-1}).

Together, these are the Nernst–Planck–Poisson equations: an entirely general description of the charge and mass transport properties of an infinitely dilute electrolyte solution. Electrolysis at an electrode surface and/or the adsorption of chemical species at surfaces can be described by boundary conditions. Homogeneous reactions, and electrolysis in porous electrodes, contribute to the mass source.

The Nernst–Planck–Poisson equations are highly nonlinear and exhibit multiple length and time scales; consequently, their full solution is rarely practical or desirable under realistic conditions, and simplifications must be sought. The most widely applicable approximation is the assumption of electroneutrality (Eq. (4)), which applies on scales larger than nanometres [2]:

$$\sum_i z_i c_i = 0 \tag{4}$$

Assuming electroneutrality and small absolute concentration gradients of charge-carrying electrolyte species, the electrolyte current obeys Ohm's law (Eq. (5)), subject to a (near-)constant conductivity (Eq. (6)):

$$-\nabla \cdot (\sigma_{soln} \nabla \varphi) = Q \tag{5}$$

$$\sigma_{soln} \approx F \sum_i z_i^2 u_i c_i \tag{6}$$

σ − conductivity (S m^{-1}); Q − charge source (A m^{-3}); F − Faraday constant; R − gas constant; T − temperature (K).

In Ohm's law, the ratio of current to electric field is the conductivity. As supporting electrolyte concentration increases compared to the reactant concentration, so the conductivity rises and the electric field tends towards zero for a given current. In the presence of excess supporting electrolyte, it is typical to assume that the concentration of the electrolyte is 'effectively infinite': mass transport of the reactant does not involve migration, and occurs only by diffusion (and convection, where relevant), as in Fick's 2nd law with convection for an incompressible flow (Eq. (7)):

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i - \mathbf{u} \cdot \nabla c_i \tag{7}$$

3. Modelling electrochemistry in COMSOL Multiphysics

COMSOL Multiphysics is designed for "multiphysics": the incorporation and coupling of diverse physical phenomena, expressed as PDEs, within one model. The desired phenomena often originate from traditionally separate fields of applied physics and engineering. One electrochemical example of a "multiphysics" problem would be fuel cell analysis, which combines fluid dynamics, mass transport, heat transfer,

and charge transfer. Multiphysics simulation can maximise physical insight and predictive power by describing accurately all relevant phenomena.

COMSOL Multiphysics implements equations using "physics interfaces". These are pre-built packages of physical equations and a choice of associated boundary conditions. Electrochemical analysis principally uses the following interfaces: Primary/Secondary/Tertiary Current Distribution, and Electroanalysis. In all of these pre-built methods, there is complete flexibility to combine and couple pre-built methods with user-defined variables or equations, as well as to alter default numerical settings (see also Section 4, below).

Both the Primary and Secondary Current Distributions treat the electrolyte current as ohmic (Eq. (5)), and solve only for electrolyte potential for a given conductivity, assuming the electrolyte composition (including the reactants) to be negligibly perturbed by electrolysis or current flow.

Primary Current Distribution requires an equilibrium (Nernstian) potential difference at an electrode surface, whereas Secondary Current Distribution allows an arbitrary electrode kinetic law to relate the Faradaic current density due to a particular reaction to its overpotential at the electrode. These interfaces have wide application in electrochemical engineering and corrosion science, but since they do not solve for reactant concentrations, they have limited relevance to electroanalytical chemistry.

The Electroanalysis interface assumes the presence of excess supporting electrolyte and so predicts a current–voltage relation by solving the diffusion–convection equation for the electroactive species (Eq. (7)). The current density will normally depend on both the potential applied at the electrode and the concentrations of the reactants at the electrode surface, according to a rate law such as the Butler–Volmer equation. This is a suitable interface for the description of many standard experimental methods, especially cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy.

Outside the approximations defined above, the Tertiary Current Distribution, Nernst–Planck interface can be used to solve the Nernst–Planck equations subject to the approximation of electroneutrality (Eqs. (3) and (4)). This includes electrolyte mass transport explicitly in the analysis, which is a computationally much more demanding problem since the equations become nonlinear. The full Nernst–Planck–Poisson equations can also be implemented by coupling of interfaces. Common applications include separation processes such as electrodialysis and the detailed modelling of batteries and fuel cells.

Other relevant physics interfaces include Laminar Flow (weakly compressible or incompressible Navier–Stokes equations) and Surface Reactions (surface adsorption and diffusion). The Transport of Concentrated Species interface implements Maxwell–Stefan diffusion to express the flux of each component species of a mixture, for cases outside the conditions where the dilute Nernst–Planck equation applies.

Heat transfer in electrochemical cells can be included using Heat Transfer interfaces, with provision for thermal conduction, convection, radiation, and predefined heat sources and sinks from electrochemical reactions, ohmic losses, and entropy changes. Further dedicated physics interfaces exist for the electrochemical modelling of lithium-ion batteries, Ni-metal hydride batteries, lead-acid batteries, electrodeposition, and corrosion. A detailed account of these interfaces exceeds the scope of this review.

4. Using the finite element method: practical considerations

The above COMSOL Multiphysics interfaces use the finite element method to solve the constituent partial differential equations (PDEs). This numerical method differs from the finite difference method, also widely applied in electrochemistry [3], since it solves the PDE in an integral (weak) form. Unknowns are discretised as sums over a set of basis ("shape") functions defined on finite elements, rather than by

discretisation of derivatives on a grid of points. The finite elements are assembled by creating a "mesh", which is a tessellation on the geometry in, for example, triangles in 2D or tetrahedra in 3D.

The chief advantages of the finite element method over the finite difference method are its adaptability to complex geometries, and the ease of handling discontinuous gradients of a variable.

To our knowledge, the last detailed discussion of the finite element method in electrochemistry was by Cutress et al. [4] (including one of the present authors), who simulated several classical electrochemical benchmarks in COMSOL Multiphysics 3.5a. Quantitative accuracy for 3D problems was found to be unachievable with the then-available meshing tools and hardware; it is interesting to note the now underwhelming prediction of "6–12 GB" memory in future desktop modelling computers. As 16 GB or larger systems are now becoming more common, the scope for 3D models continues to grow with hardware power.

Like any discrete numerical method for solving a continuous PDE, the finite element method introduces some numerical error; to minimise this, it is necessary to use an appropriate mesh. A numerically stable finite element solution converges to the analytical result with naïve, global mesh refinement, provided sufficient hardware is available.

Significantly more efficient, however, is to refine the mesh locally, on the basis of the likely regions where flux gradients (e.g., diffusive flux) change rapidly. In diffusive problems, it is particularly important to refine the mesh locally to singularities where the flux may be infinite or ill-defined, such as at the circumference boundary of a microdisc electrode where electroactive and insulating surfaces meet.

COMSOL Multiphysics allows mesh size and element-to-element expansion rate to be explicitly controlled at any point or on any boundary or volume within a model. The mesh must conform to all geometric features (faces, edges, etc.), so the reported failure to resolve small objects (Fig. 1a, [4]) is no longer a concern.

The COMSOL® Model Library example "Voltammetry at a Microdisk Electrode" [5] uses the analytical steady-state current at a microdisc electrode as a benchmark for required mesh refinement. To achieve 0.7% accuracy in a 2D axisymmetric model, the mesh is refined to $r_e/100$ at the electrode radius $r = r_e$, and the global element growth rate is limited to 1.1.

The authors created a single quadrant of a 3D microdisc geometry using COMSOL Multiphysics 4.4. The same mesh settings as the 2D example gave 0.8% accuracy, compared to the analytical result; this mesh contained 4×10^5 elements. The steady-state concentration profile was computed for a single species in the mass-transport limit in 11 s, using all four cores of an Intel Xeon E31225 3.1 GHz with 16 GB RAM. Less than 2 GB RAM was actually required, with the default solver. A refined mesh with 3×10^6 elements gave 0.5% accuracy, taking 1 min and using 4 GB RAM.

COMSOL Multiphysics also supplies an "adaptive" mesher to automatically refine the mesh in the required regions. The authors found that 20 iterations of adaptive mesh refinement on the 2D microdisc problem yielded <0.1% error compared to the analytical solution, albeit over a longer runtime than for a user-controlled mesh. Klymenko et al. [6] discussed critically the scope of adaptive meshing in the context of reaction fronts.

Mapped spaces are not usually employed in built-in methods for COMSOL Multiphysics. "Infinite elements" can be used to project a finite simulation space 'to infinity' in order to describe, for example, a hemispherical infinite expanse of bulk solution without needing a simulation space of excess size compared to the electrode [5].

For the interfaces described above, time-dependent problems are solved by integration of the PDE in time according to an implicit backwards differentiated formula (BDF) method [7]. The COMSOL Multiphysics solver automatically chooses appropriate numerical time steps. These are set to be as long as possible within a certain relative or absolute tolerance for the accuracy of the integration, which is estimated during runtime. The dedicated Electroanalysis interface enabled

the tuning of solver tolerances to resolve voltammetric events, mitigating issues such as "spiking" of voltammetry due to fast follow-up kinetics [4].

5. Historical review of finite element software for electrochemical analysis

The literature from the last four years suggests that the majority of recent applications of COMSOL Multiphysics in analytical electrochemistry involve one or more of the following: non-standard or complex geometry; hydrodynamic electrochemistry; or, multiple or complex reaction chemistry, whether hetero- or homogeneous.

All of these phenomena imply a theoretical description that cannot necessarily be implemented straightforwardly in existing commercial tools for electroanalysis, at standard geometries (planar electrode, microdisc, etc.) or under standard conditions. Moreover, numerical concerns may make such theory challenging for the researcher to implement in code. In such cases, electrochemical research benefits from the flexibility of general-purpose commercial software providing a broad scope for numerical analysis across a range of physical conditions.

Where not stated otherwise, the theoretical work reported in this section was achieved using COMSOL Multiphysics.

5.1. Complex geometry

The investigation of Godino et al. [8] into chronoamperometric transients at electrode arrays eschewed the usual diffusion domain approximation [9] (reducing a 3D problem to 2D axisymmetry; hereafter, DDA) and treated the problem as three-dimensional. This is geometrically exact, but had traditionally been viewed as inaccessible for reasons of computational problem size.

Lavacchi et al. [10] solved for inlaid and recessed microdisc arrays with the DDA. They emphasised the need for care with meshing while also highlighting the flexibility of the approach. The recessed microdisc and microwell problem was addressed more recently by Oleinick et al. [11], who considered the action of a "diffusional Faraday cage" in a generator-collector mode sensor design. Thin layer effects at gold micropillars have also been studied [12] and compared to experiment with good agreement. Odijk et al. [13] modelled "differential cyclic voltammetry" for redox cycling at interdigitated electrodes.

Other non-standard geometries in electroanalysis have included crystals and electroactive nanoparticles. Claussen et al. [14] modelled diffusion–reaction systems (with DDA) to gauge the influence of mass transport effects on the efficacy of nanoparticle-catalysed biosensors. Unwin and co-workers have considered dissolution kinetics of calcite crystals in acidic solution [15,16] including the implications for local surface measurement techniques such as scanning ion-conductance microscopy [17].

5.2. Complex chemical mechanisms

Sartin et al. [18] implemented a complex chemical kinetic scheme in COMSOL Multiphysics to determine concentration profiles in electrochemiluminescence (ECL). The theory required the flexibility to introduce an arbitrary kinetic scheme and arbitrary transient voltage loads. Klymenko et al. recently revisited ECL analysis [19], using COMSOL Multiphysics to verify their KISSA software. The authors reported relatively poor runtime compared to their own, specialised code, and re-iterated the need for care and electrochemical experience in model setup.

Scanning electrochemical microscopy (SECM) combines a sometimes complex electrochemical system with a non-standard geometry. Examples of theoretical work include the response to an EC' mechanism close to an SECM tip [20] and tip-position modulation with a moving electron transfer site [21]. Zhou et al. simulated approach curves for an electrochemically heterogeneous substrate to demonstrate the

differentiation of active sites within an in-plane matrix of lower reactivity [22].

5.3. Hydrodynamic electrochemistry

In 2011, Santillo et al. reviewed hydrodynamic electrochemistry simulation with COMSOL Multiphysics [23]. The coupling of mass transport with flow has been considered in a methodology and design optimisation for flow sensing by Amatore et al. [24]; the same authors modelled chronoamperometry at a channel electrode [25] using the finite element method.

Amatore and Thouin also collaborated to solve a modified diffusion(-convection) equation to reveal the effect of natural convection in microdisc [26] and channel flow microband [27] geometries, with experimental corroboration.

Torrents et al. [28] considered sensing using channel flow electrodes, modelling a microfluidic respirometer incorporating oxygen amperometry to infer biological oxygen demand. This study combined electrolysis with homogeneous enzyme kinetics in solution; Bitziou et al. [29] used a similar coupling to study ascorbic acid oxidation in a flow.

5.4. Miscellaneous

The solution of the diffusion equation in a two-phase system has been applied to consider stripping voltammetry [30] and cyclic voltammetry with ion transfer for an ITIES system [31].

Vasquez-Arenas et al. [32] included simulation in a simple student voltammetry experiment, highlighting its role to better inform the relevant theory and reasoning surrounding the experimental approach.

6. Conclusion

Partial differential equations resulting from standard approximations in electrochemical theory are implemented in COMSOL Multiphysics using built-in "physics interfaces". These interfaces provide full access to the equations and permit flexible, user-controlled physical configurations for the description of electrochemical systems.

COMSOL Multiphysics is widely applied in electrochemistry, especially for non-standard theoretical analysis. Wherever dedicated electrochemical software cannot be relied on, or where in-house code becomes awkward to maintain or develop, the ease of implementation afforded by general-purpose software can aid the researcher in rapidly obtaining theoretical results, subject to an easily controlled range of approximations.

Klymenko et al. [19] have noted that "approaches based on Comsol [*sic*] lead to excellent results under specific circumstances, [but] they rely on profound expertise from their potential users, and hence, may easily lead to erroneous predictions in the hands of novices." While the latter remark is certainly true, any numerical method can yield unreliable conclusions in the hands of users with inadequate electrochemical experience to interpret numerical results in their proper context.

Errors associated with the finite element solution of equations can be minimised with care in the physical configuration of the problem and when meshing. As with any numerical method, convergence analysis is required to establish the magnitude of numerical errors due to discretisation [33]. The ease of implementation of a model using pre-built interfaces in commercial software does not absolve the user of responsibility for affirming the physical reasonableness of their results.

COMSOL Multiphysics allows control of physical equations and numerical settings, while providing judicious automated defaults for meshing and solver configuration. The aim of this approach is to allow expert electrochemists to undertake theoretical work, without demanding expert knowledge of numerical analysis. Within this environment, we hope that electrochemistry will benefit from informed application of finite element software.

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