Simulated curves compared to recorded data have provided a breadth of insight into mechanisms and kinetic aspects of charge transfer at the liquid|liquid interface (LLI). This is often performed with software employing finite element methods (FEMs). The advent and application of this asset to soft interfacial chemistry has allowed a more facile exploration of geometric considerations, the role of interfacial size (from macro to nano), while simultaneously expanding to include homo/heterogeneous reactions such as electrocatalytic, photochemical, nanoparticle interactions, etc. This article provides insight into the status of the field of LLI FEM studies as well as a perspective as to what role simulations and numerical analysis will play in the future.

Introduction

Finite element method (FEM) simulation software is ultimately a synthesis of established analytical equations with geometric components. These can then contain complex material properties or be combined with multiple physics (so-called multi-physics), or equation sets, e.g. heat transfer with electrical conduction. The degree of complexity of these systems necessitates their numerical simulation. To facilitate this, the geometry is subdivided by a mesh consisting of elements, e.g. free triangular or quadrilateral. In this discretization, the problem is then solved for each element and subsequently compared to the whole. FEM has been an invaluable utility for electrochemists in battery, materials, mass transport problems, etc. and has been comprehensively reviewed [1–3]. More complex simulations of electrochemical systems, for example by molecular dynamics or by density functional theory, are outside the scope of this article.

Electrochemistry at interfaces between two immiscible electrolyte solutions (ITIES) is a distinct and versatile area of contemporary electrochemistry, as summarized by recent reviews [4–9]. This review will focus on digital simulations of electrochemical processes at ITIES, highlighting the applications as well as the perspectives. Scheme 1 illustrates the development of a simulation from the experiment, in this case an interface held at the tip of a pipette – a micro-ITIES, as well as mesh refinement. Refining the mesh can be a particularly challenging aspect of the FEM; too fine and run-times become prohibitively long, too coarse and the result is not accurate or precise. Great care should be given to this step, with comparison using simple mechanics to known analytical solutions before moving forward with more exotic systems.

Charge transfer simulations at an ITIES

While conventional electrochemistry operates at a solid|liquid interface, e.g. metal (Pt, Au, etc.) or carbon, fundamentally analogous charge transfer reactions can take place at LLI s such as water|oil (w|o), or even w|ionic liquid (w|IL). This means that the same electrochemical techniques (e.g., cyclic voltammetry (CV)) and theory of charge transfer can be transposed to so-called soft interfaces. This is advantageous as LLI electrochemistry is not limited to redox electrochemistry, but also includes simple and facilitated ion transfer (FIT) reactions, where ions are pushed or pulled across an interface. Simple ion transfer (IT) of ion i with charge z transferring from water (w) to oil (o) is given through the following reaction:

$$i_w \leftrightarrow i_o$$

(1)

Ions are manipulated by biasing the potential across the ITIES using electrodes immersed in either phase. The potential drop is localized across the w|o interface (~1 nm) and called the Galvani potential difference ($\phi_w - \phi_o = \Delta \phi$); where $\phi_w$ and $\phi_o$ are the potentials in...
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Scheme 1

(A) schematic of a micropipette ITIES experimental setup; (B) photograph of the pipette tip immersed in an organic phase (o) with an aqueous (w) solution held inside and the interface at the tip; (C) the pipette tip converted to 2D axial symmetric geometry, taking advantage of the infinite rotational symmetry C∞h element of the cylindrical capillary and further reducing it in half greatly reduces the computational effort and simulation run time; (D) illustrates the mesh surrounding the simulated ITIES shown in C, where an additional geometry element, a box, has been added to better refine the mesh in the area of hemispherical diffusion in the vicinity of the ITIES on the o side.

The aqueous phase w and o, respectively. \( \Delta_{\text{w}} \phi \) is controlled via electrodes positioned in either phase. In this way, \( \Delta_{\text{w}} \phi \) is similar to \( E \) or the potential drop across a solid|liquid boundary and the kinetics of IT are often handled using a Butler–Volmer model [4]. These equations often form the basis for most simulations, which can then be expanded upon for further complexity. Indeed, the driver for digital simulations is often the absence of a simplified analytical solution.

**Fundamental studies**

Dropelt or thick-film modified electrodes are one macro-ITIES (mm² to cm²) system often simulated, with electron transfer (ET) across the electrode-droplet interface coupled to IT across the LLI. Zanotto et al. [10*] recently explored a solid electrode completely covered by a thick organic film, which was then immersed in an aqueous phase, using a 1D simulation. They showed [10*] that the coupled effect of ET at the solid|o interface with IT at w|o had an appreciable influence on the shape, peak-to-peak potential difference, as well as the mid-peak potential in the \( i-V \) curve. The numerical simulations could satisfactorily explain deviation from the 59 mV peak-to-peak separation expected for a reversible ET or IT reaction (number of electrons \( z = 1 \) for ET or singly charged species for IT). This approach is actually similar to typical ionophore-based ion-selective electrodes (ISE) [11], where a solid conducting polymer is used for ET that is coupled with transfer of an analyte ion across the water-membrane interface. Simulations of these kinds have been considered by Lewenstam utilizing Nernst–Planck–Poisson equations [12], and by Amemiya [13,14] and Bakker’s groups [15*,16] for the fully electrolyte supported case; i.e. Fick’s laws of diffusion.

These simulations were extended to 2D to study coupled ET–IT reactions upon collision of organic droplets with an electrode [17*], considering both diffusion and migration. In this case, the secondary or tertiary current distribution was also solved to show that the jR drop in the toluene solution is negligible. Furthermore, both the entire electrode|o and w|o surface are electrochemically active, despite higher current densities at the three-phase boundary. From comparison with the experimental data, it was apparent that the colliding droplets had quite high contact angles with the electrode after collision.

Meanwhile, the exact mechanism of ET across LLI has been a subject of controversy [2]. This topic was recently revisited by a combination of experiments and FEM simulations of ET between ferrocene (Fc) and hexacyanoferrate (FeCN₆⁴⁺) [18*]. Comparison with experimental and simulated CVs indicate that the likely mechanism is one of potential independent Fc partitioning to w with subsequent Fc oxidation/FeCN₆⁴⁺ reduction in the bulk aqueous phase, followed by potential-dependent Fc⁺
transfer back from $\omega \rightarrow \sigma$. These data agree well with the earlier experimental and simulated results of Osakai and co-workers [19]. If a gold nanofilm was added to the interface, it behaved as a bipolar electrode and electrons were shuttled through the gold film in a heterogeneous interfacial redox electrocatalysis [18*,20]. Stockmann et al. [21*] exploited the Pt nanoparticle catalysis of O$_2$ reduction at a LLI for single nanoparticle impact studies; whereby, as a nanoparticle impacts with the interface a spike from the electrocatalytically enhanced reaction is recorded in the current transient in the pA range. Nanoparticle simulations [21*] at the LLI were used to explore the effect of penetration depth, through a symmetrically bifurcated sphere cap and superhemisphere, on the spike current intensity. These simulations also confirmed the necessity of an O$_2$ partitioning mechanism – between water and 1,2-dichloroethane – proposed by Trojánek et al. [22].

1D simulations have provided insight into differential capacitance at the back-to-back double layers formed when a LLI is established. These showed that the width and symmetry of the two interfacial regions are crucial parameters and experimental capacitance data could be used to estimate the width of the interfacial region, which the authors suggest is on the order of 3 nm [23]. FEM was also used to calculate the current distribution in a large rectangular cell with smaller electrodes, ruling out the current distribution as an explanation for the driving force for a Marangoni shutter where gold nanoparticles, adsorbed at the ITIES, move to the center of the cell and to the edges as a function of the applied polarization [24].

Additionally, FEM have been utilized for detailed characterization of a flexible thin layer electrochemical flow cell for ultrasensitive amperometric detection at an ITIES, reaching nanomolar detection limits [25]. If ITIES-based devices become more common, this kind of simulation will be extremely useful for device optimization. The recent use of macro scale (mm$\rightarrow$cm) models [10*,16,18*,26*–29] suggests that there is a thriving field of study for bulk material properties, their interaction with the LLI, and the fundamental interrogation of the LLI’s physical properties.

With the rapid development of modern micro [30,31], and nano fabrication techniques [32,33], there was a push toward miniaturization owing to a number of benefits. These included reduced capacitance/solution resistance due to the lower operational current range and thus, no longer required $\text{R}^\text{R}$-compensation. This meant that the interfacial surface (e.g. radius of a disc interface) was smaller than the diffusion layer thickness ($\delta \approx (D\tau)^{1/2}$) at most scan rates and hence steady state current profiles were generated. This improved mass transport increased the experimental sensitivity permitting the exploration of faster charge transfer reactions and had a concomitant interest toward their characterization through simulation. A recent perspective by Arrigan and Herzog [8*] in this journal examined simple IT and so the concept is only briefly introduced here. Additionally, electrochemistry at macro, micro, and nano interfaces has been reviewed recently [7,9]. One of the first simulations by Girault’s group [34] focused on the position of the LLI at a micropore; on either side or within a microchannel. Later, pore angle and spacing were explored for micro-ITIES arrays by Arrigan’s group [35,36]. This was extended to interfaces housed at the tip of pulled borosilicate or quartz glass capillaries [37,38]. Nishi et al. [37] examined the geometric effect combined with a viscous secondary phase, specifically w/IL vs. w/o interfaces, where the diffusion coefficient is 3–4 orders of magnitude lower for the former vs. the latter. This causes the $i$–$V$ profile to resemble a macro-ITIES signal with linear diffusion dominating in both IT directions owing to the increased viscosity in the IL phase, whereas $\omega$ diffusion is confined by the pipette walls. In 2009, Rodgers et al. [38] examined the effect of taper angle on pulled quartz pipettes, the diffusion of species, and the resultant $i$–$V$ signal. They demonstrated that forward and reverse waves could characterize the geometric and transport properties of the pulled pipette [38] with a high degree of sensitivity. Simultaneously, micro LLI arrays have been developed and explored, e.g. Alvarez de Eulate et al. [39], with the goal of understanding interface location and its impact on $i$–$V$ curves.

The complexity of these models was increased to examine FIT processes with typically 3–4 processes being considered [5]. This has led to studies at the $\omega$/IL interface [40] where ILs have been shown to be excellent solvents for metal ion extraction, but also the utility of somewhat exotic organic solvents, like CHCl$_3$ [41]. In the latter [41], a phospholipid, 1,2-dimyristoyl-sn-glycerol-3-phosphocholine (DMPC), highly soluble in CHCl$_3$ ($\varepsilon = 4.81$), was investigated at a blunt pulled micro-ITIES ($\Omega = 25 \mu m$). This confirmed that the analytical solution of FIT, formulated for a macro-ITIES, was transposable to the micro-ITIES platform employed.

**Electrocatalytic reactions**

Owing to its biomimetic nature, there are a number of valuable electrocatalytic reactions such as the O$_2$ reduction reaction (ORR) that are of considerable interest. This is exemplified through the recent work by Girault’s group [26–28], examined through a macro-ITIES 1D simulation. Therein, Girault and co-workers examined the ORR (see Figure 1) using decamethylferrocene (DMFc), and other metallocenes as catalyst/electron donor in the oil phase and H$_2$SO$_4$ as the proton source in the aqueous phase. Protons are pushed across the interface at high positive potentials and coordinate with DMFc in the bulk oil phase in the vicinity of the ITIES. While the DMFc hydride formation, and subsequent oxidation, were treated as bulk processes, the speed of the reaction in-
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Figure 1

Mechanism of O₂ reduction using decamethylferrocene as both electron donor and catalyst, while the liquid|liquid interface, between water|1,2-dichloroethane (w|DCE) acts as the junction for charge separation.

Source: Adapted from Journal of Electroanalytical Chemistry, Vol 729, Stockmann TJ, Deng H, Peljo P, Kontturi K, Opollo M, Girault HH, Mechanism of oxygen reduction by metalloccenes near liquid|liquid interfaces, Pages No.43-52, Copyright 2014, with permission from Elsevier [27].

dicated that the reaction layer was small, ∼50 μm, compared to the diffusion layer thickness without O₂ reduction, ∼200 μm [27]. Simulated and experimental CVs were compared through two curve features: (i) the absence of a proton return peak in the edge-of-scan profile and (ii) the DMFc⁺ transfer peak intensity. Through a similar process, this group examined the surprising O₂ reduction at LLIs in the presence of alkali metals or rather their hydration sphere, whose protons are made acidic as they transfer across the ITIES [28,29].

Optimizing or predicting the reaction layer thickness of a system is a valuable utility when trying to incorporate additional in situ detection methods to complement the electrochemical ones, such as electrogenerated chemiluminescence, scanning electrochemical microscopy (SECM), etc.

SECM simulations

SECM digital simulations have been utilized extensively for LLIs. For example, H₂O₂ generated from O₂ reduction by DMFc at a trifluorotoluene|water (TFT|w) interface was probed by a SECM tip sensitive to H₂O₂, and the experimental results were compared with FEM simulated curves. If the H₂O₂ generation was modeled as a constant flux from the ITIES, simulations show negative feedback close to the interface, while the experiments show continuous increase also close to the interface. Hence, a model considering H₂O₂ generation within the 50 μm thick uniform reaction zone was considered to obtain better agreement with the experimental data [42].

Mirkin and co-workers proposed ET/IT as a new mode of SECM operation, using a nanometer sized pipette filled with an organic phase containing a neutral redox mediator [43]. This redox mediator can partition into the aqueous phase and undergo redox reactions at the substrate. The ions produced in this ET reaction can be transferred into the organic filling solution of the nanopipette in an IT reaction, giving rise to a measurable IT tip current. Transfer of other ions at the tip can be used for distance control in negative feedback mode. Digital simulations were employed to study the ET/IT feedback considering (i) the partitioning of neutral redox species from the pipette to the external solution, (ii) diffusion of these species to and their oxidation (or reduction) at the conductive substrate, (iii) diffusion of the reaction product to the pipette orifice, and (iv) IT at the tip ITIES. This approach was later used to detect short-lived intermediates of electrocatalytic O₂ reduction, by using O₂ as a redox mediator for the ET reaction, and measuring the IT current of the O₂⁻ intermediate [44]. Additionally, simulations can be used to generate analytical approximations, as done recently by Oleinick et al. [45**] for the ET/IT SECM configuration where the surface-generated ionic species is either chemically stable or participates in a first- or second-order homogeneous reaction.

Furthermore, digital simulations of SECM have been used to study the kinetics of O₂ reduction by DMFc in acidified DCE in an EC mechanism, where DMFc generated at the SECM tip reacted homogenously with O₂ and protons to regenerate the initial DMFc⁺. Through comparison of simulated and experimental curves an apparent rate constant for the homogeneous reaction was obtained [46].

Nanopores fabricated in a nanocrystalline silicon membrane have been probed by SECM with a high degree of resolution achieved through the use of a nanopipette [47,48]. FEM simulation was employed to investigate the spatial resolution of the approach [47]. This report has interesting implications toward biological cellular imaging particularly when combined with the following: (i) the recent work by Kuss et al. [49] that used high speed SECM imaging with a Pt disc micro electrode in conjunction with a forced convection numerical model to study the redox properties of live cells; (ii) as well as the work of Henderson et al. [50] in the development of a 3D topographical simulation for their live cell investigations. The combination of these three works suggests one direction SECM and numerical analysis could take. That is, rapid bio-imaging of cells using liquid|liquid junction scanning
probes with a high degree of spatial resolution. With this, a more comprehensive picture of bio-cellular processes could be gained in conjunction with the simultaneous response of live cells to external stimuli. The LLI offers the possibility to investigate living cells using non-redox active charged species. This is demonstrative of one potential avenue for FEM simulation development and application.

Multiphysics approach
Ovejero et al. have studied the effect of forced hydrodynamic convection on both IT and FIT, both theoretically and experimentally [51]. This is an example of a typical approach where the fluid velocity was assumed independent of the distance from the stirrer [51]. This assumption is reasonable if the electrode distance from the stirrer is large enough, reaching a constant value of $0.88447 \times \sqrt{\omega}$, where $\nu$ is the kinematic viscosity and $\omega$ is the angular velocity of rotation, as demonstrated by Levich [52]. Additionally, hydrodynamic conditions produced by the rotating stirrers are comparable to those of the rotating-disc electrode at long distance [51]. These kinds of models are relatively easy to solve, but the model accuracy can be rather limited. However, recent development in both computer hardware and software has made more complex models accessible even on tabletop computers. For example, recently Vega Mercado et al. proposed a novel electrochemical methodology to determine the partition coefficient of neutral weak bases [53*]. In this case, forced convection by a rotating rod in the top phase was used to enhance the mass transfer to and from the top phase, and the relationships between charges transferred during the forward sweep of the CV at different rotation rates and at different pHs allow determination of the partition coefficients of weak bases. Models of varying complexity were developed to validate the methodology, whereas magnetic resonance imaging (MRI, also sometimes called nuclear magnetic resonance (NMR) imaging) was utilized to experimentally validate the computational fluid dynamic (CFD) simulations, both in 2D and 3D. This article is an example of the complex combination of both CFD simulations with those of mass transfer in two phases, acid-base reactions, partitioning of neutral species, and potential controlled IT. The discrepancy between the simulated and experimental velocity values show that further development is still required especially for 3D modeling, but the trends are reproduced remarkably well, as shown in Figure 2.

Moving boundary model was utilized by Oseland et al. [54*], who used a 1D FEM model to study amine (jelfamine D230) transfer from an expanding droplet into an aqueous solution. Microelectrochemical measurements at expanding droplets were used to probe the potentiometric response of a pH sensitive microelectrode, and this response could be converted to give the concentration profile of the amine as a function of the electrode-
droplet separation when the measurement was coupled with time-lapse microscopy. The theoretical concentration profile obtained with a moving plane model in COMSOL to describe the expanding droplet matched well the experimental data [54*]. Moving boundaries are important for applications where shape and size of the droplet changes over time, for deposition of solids at LLI etc. and further development is expected to see these models utilized for understanding these effects better. For example, the shape of a droplet on an electrode depends on the applied potential, so digital simulations corroborated by experiments would be beneficial for understanding the electrochemical response upon droplet collision with an electrode.

Furthermore, a fundamental question that is still of importance is the adsorption of species at an ITIES and in the vicinity on the material walls of electrolytic cells. This has previously been explored by Méndez et al. [55] using a Guoy–Chapman model for species adsorbing at the interface, while Ellis et al. [56] examined species adsorbing on the pore wall of a micro-pore ITIES through a Langmuir
model. It would be interesting to combine these two perspectives as well as include other phenomena, like photocatalytic processes or the influence of adsorbed nanoparticles.

**Photochemical charge transfer reactions**

Another example of utilizing multiphysics digital simulations was demonstrated by Méndez et al. [57] for investigating photochemical reactions at LLIs under hydrodynamic convection in a system for conversion and storage of solar energy: photo-ionic cells. The solar energy is converted to chemical energy in a homogenous photochemical reaction between a sensitizer and a quencher, and stored by extraction of the photoproduct into the organic adjacent phase (as shown in Figure 3A), followed by physical separation of the phases. The energy can be recovered electrochemically with a biphasic fuel cell to produce electricity on demand [57]. Photochemical reactions have a large number of parameters affecting the quantum yield and efficiency of the system, so digital simulations are useful to pinpoint the most critical ones for further optimization. This requires coupling of simulations for both the light absorption and the mass transport of reactants, as well as computational fluid dynamics to account for the fluid flow; some results are illustrated in Figure 3B–D [58*]. The FEM simulations were used to evaluate the conditions required to reach large quantum yields of over 50%; long excited state lifetime (in the order of 10–100 μs), large partition coefficient for the hydrophobic photoproduct, reasonable dye concentrations and large redox potential difference between the sensitizer and the quencher [57]. The simulations also show that the photoreaction should take place very close to the LLI to minimize the diffusion lengths and time to avoid recombination reactions. Further simulations were performed to evaluate the effect of the droplet size on the attainable quantum yield [58*]. These papers give an example of utilizing digital simulations for “debottlenecking”, where the effect of the different parameters are evaluated to give guidelines about what is required to achieve high utilization of light.

**Conclusions and perspectives**

This review has shown that digital simulations have been utilized to analyze experimental results involving interfacial charge transfer reactions, moving interfaces, partition and complexation of species, photoreactions and forced hydrodynamic convection.

As computational power further increases and the requisite cost (in terms of both time and monetarily with regards to computational processing power and memory) becomes more affordable/achievable, the use of simulation software toward geometric, materials, etc., problems will become more ubiquitous and further exploit the ‘multi-physics’ aspect. That is to say, the inherent power of this method is not only to merge geometric and mass transport properties together, but is likely to expand to incorporate the interaction of other physical parameters, e.g., capacitance models, surface tension (e.g. through moving boundary), as well as nanoparticle interactions, etc., not to mention 3D aspects, pushing the frontier understanding and physical insight of complex processes of LLI systems.

As stated in the review by Arrigan and Herzog [8*] about miniaturized ITIES: “truly comprehensive models that incorporate mass transport, kinetics and capacitance, to
enable a complete characterization of a system under dynamic electrochemical conditions have yet to appear”. This review indicates that significant progress has been made in comprehensive modeling, and this trend will continue. However, it should be stressed that careful care has to be taken with simulations, and verification against experimental and analytical solutions should always be performed.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

● Paper of special interest.
● Paper of outstanding interest.


12. Theory of coupling of ET-IT reactions at thick-film modified electrodes, how these two processes interrelate, particularly with respect to the resultant J-V signal.


19. Interrogation of the ET mechanism of the FeC/Fe(CN)64– across a LLI showed that it occurs as a bulk process in the w phase with the observed current originating from the IT of the oxidised FeC+. If a nanofilm is introduced, it behaves as a bipolar electrode and the mechanism ET becomes heterogeneous.


Example of utilising digital simulations for understanding electrocatalytic reactions at liquid–liquid interfaces.


54. Partitioning of neutral bases at a macro w/o interface under forced hydrodynamic conditions is modelled and correlated by multiple analytical techniques.


56. Partition of an amine is investigated at an expanding oil–water droplet using a microelectrode and modelled with a moving boundary.


Example of simulations of mass transfer, light adsorption and photo-reactions, and hydrodynamics for evaluation of the system performance.