Computation of Forced Convection in Electrochemical Cells Installed in a Sudden Expansion

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Abstract

After successful results obtained from a developed code aiming at the computation of natural and forced convection in electrochemical cells, there is a possibility to develop it to sudden expansion case. In such case the verified code has been extended to the prediction of in a binary electrolyte solution of multi-ion electrochemical reactor with sudden expansion geometry. The concentration, current density, turbulence structure and the development of boundary layer has been numerically predicted in non-pervious obtained results.

Keywords: forced convection; Multi-ion; Finite volume method; Turbulent Mass transfer; Current density distribution

1. Introduction

Electrochemical cells appear in several industrial applications, such as copper refining cells and lead-acid batteries. Natural convection induced by variations of ionic concentration plays on essential role in electrochemical cells. It turns out that between the different transport mechanisms, convection, migration and convection controls in most applications. The fact that the liquid moves due to buoyancy influences the mass transport process considerably. The efficiency of the transport mechanisms in turn directly influences the process of interest in the cell. Hydrodynamics of electrochemical cells have been subject to many scientific and industrial investigations in the past few years. In general, ionic mass transfer is based on three different transport mechanisms, as outlined in Newman and Thomas-Alyea [1]: ionic mass transport as a result of a velocity field (convection), mass transfer as a result of concentration gradients (diffusion), and mass transfer as a result of an electric field (migration). In electrochemical cells, local density variations are caused by local variations of the ionic concentration. Such concentration gradients occur especially near electrode surfaces, where electrochemical reactions take place. In the case of a weak influence of forced convection, natural convection can have significant effects on the reaction rates along the electrodes or on the limiting currents. The influence of natural convection in electrochemical cells was already considered theoretically and experimentally in the year 1949 in Wagner [2]. The

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influence of natural convection on the current distribution along the cathode and on the limiting current was investigated based on the boundary-layer theory [2]. The effect of migration on the limiting current in the presence of supporting electrolyte was studied in Selman and Newman [3]. Concentration and velocity profiles near vertical electrodes were investigated, e.g., in Awakura et al. [4] and Fukunaka et al. [5]. Local current density distributions along the cathode were studied, by Awakura et al. [6]. Recently, concentration profiles were measured experimentally by interferometry in Yang et al. [7].

In Chung [8], the tertiary current density distribution in the case of multi-ion electrodeposition was studied for high-aspect-ratio cells including convection, diffusion and migration. The flow, the ionic concentration and the potential field were strongly coupled by an iterative (two-dimensional) finite volume scheme. Natural convection phenomena were also investigated inWallgren et al.[9]] using a finite volume scheme, including an ion-transport equation for binary electrolyte solutions, an equation for the electric potential and the Butler-Volmer law as a kinetic boundary condition. Andreas et al. [10] has presented a novel computational approach for the numerical simulation of electrochemical systems influenced by natural convection phenomena. A stabilized finite element framework for multi-ion transport mechanisms including convection, diffusion and migration coupled to an incompressible flow solver has been developed. The role of a galvanostatic Butler-Volmer condition including the interaction of ionic concentration at the surface of the electrode and the surface overpotential was emphasized, to obtain a non-uniform surface overpotential distribution. Additionally, a three-dimensional rotationally-symmetric boundary condition was used for modeling rotating cylinder electrodes. The computational framework was tested for various numerical examples exhibiting two- and three-dimensional electrochemical cell configurations including dilute $CuSO_4$ electrolyte solutions with and without excess of supporting H_2SO_4 electrolyte.

Over the last decades, various numerical approaches for the simulation of multi-ion transport in dilute electrolyte solutions were developed; in the following, some of these approaches will be addressed. In Kwok and Wu [11], a fractional-step algorithm using a finite- difference scheme for spatial discretization was proposed. Steady-state studies for a two-dimensional parallel plane flow channel were performed in Bortels et al. [12] using a new multi-dimensional upwinding method for the analysis of multi-ion electrolytes controlled by diffusion, convection and migration. A finite-difference method with upwinding was developed in Georgiadou [13] for the simulation of convection-dominated multi-ion transport. Using that method, various two-dimensional electrochemical problem settings including convection were studied (see, e.g., Georgiadou [13, 14] and references therein). In Barak-Shinar et al. [15], a three-dimensional model of an electrochemical sensor was investigated. A finite-volume software package was used for solving the Nernst–Planck/Poisson–Boltzmann system of equations coupled to the Navier–Stokes equations. A finite-volume method for solving three-dimensional diffusion-migration problems on irregular domains with moving boundaries was proposed in Buoni and Petzold [16]. Georg Bauer et al. [17] have presented a new finite element approach to the numerical simulation of electrochemical systems including all multi-ion transport mechanisms (convection, diffusion and migration).

A novel stabilized finite element method derived from the variational multiscale method for the numerical simulation of multi-ion transport in dilute electrolyte solutions has been developed in Georg Bauer et al. [18]. Volgin et al. [19, 20] have performed multi-ion calculations using the finite difference method. Most of the examples presented were rather theoretical, but some interesting comments on the stability and solution speed of the multi-ion equations were made. However, all the results presented by Volgin et al. [19, 20] mentioned above are limited to laminar flow conditions. Numerical treatment of turbulent mass transfer is almost always supposed to be analogous to turbulent heat transfer, see Newman and Thomas [1] and Notter and Sleicher [21] and Churchill [22]. Schmidt number of the reaction ions, characterizing mass transfer, is at least thousand times higher than the equivalent Prandtl number for heat transfer. Therefore, the concentration boundary layer is much thinner than the hydrodynamic or thermal boundary layer,

leaving the numerical treatment of turbulent mass transfer in arbitrary geometries far from easy, well established and understood in Nelissen et al. [23].

Several authors Wang [24] and Rosen and Traegaardh [25] have presented results of mass transfer at a high Schmidt number in turbulent flow. These contributions were either based on a boundary integral method to obtain the results in the boundary layer or solve only the convection–diffusion equation, including the turbulent diffusion, to obtain the limiting current situation.

Gurniki et al. [26, 27] calculated turbulent mass transfer in nonlimiting current situations. They studied the use of large eddy simulations (LES) for predicting turbulent mass transfer in a parallel plate reactor, taking into account the turbulent fluctuations of the concentration. Only a binary electrolyte is considered which allowed the solution to be obtained in terms of one equivalent concentration $C = Z_1 C_1 = Z_2 C_2$. In order to model turbulent mass transfer, the turbulent fluid flow needs to be calculated. Nelissen et al. [28] solved the multi-ion transport and reaction model in turbulent flow. The model describes the effects of convection, diffusion, migration, chemical reactions and electrode reactions on the concentration, potential and current density distributions in an electrochemical reactor. The Reynolds averaged Navier–Stokes (RANS) equations were used to calculate the turbulent flow, with the turbulent viscosity obtained from a low-Reynolds number $k - \omega$ model. Different turbulence models for the turbulent mass transfer were examined and validated in a parallel plate reactor for the deposition of copper (Cu) from an acid copper-plating bath. The most accurate turbulent mass transfer models were the algebraic model for the turbulent diffusion and the newly suggested model with the constant turbulent Schmidt number equal to 4.5 by Nelissen et al. [28]. Experimental and numerical studies on the dynamics of flow and mass transfer in a tubular electrochemical reactor with cylindrical a mesh electrode were concerned by Ibrahim et al. [29]. The study was aimed for wastewater treatment. An improvement of the reactor only performance has been reached with higher flow rate.

The objective of the research is to a theoretical extending of a validated code developed by the present author to simulate sudden expansion. The model describes the effects of convection, diffusion, migration, chemical reaction and electrode reaction on the concentration, potential and current density distribution in an electrochemical reactor. The Reynolds averaged Navier–Stokes (RANS) equations are used to calculate the turbulent flow case using the standard $k - \varepsilon$ (STD) model. In order to generate a decision on the quality of the code, the computational results are compared with available experimental data and with previous simulations.

2. Mathematical Model
2.1. Governing equations

In the present work, Multi-ion in a dilute electrolyte solution is considered for the time. The incompressible Navier-Stokes equations provide an adequate model to describe the flow of a multi-ion electrolyte solution in an electrochemical cell and the standard $k - \varepsilon$ (STD) model will be chosen to be an adequate turbulence model to represent the turbulence parameters and ionic species transport equation. These equations and boundary conditions have been emerged in [30].

3. Numerical examples

Figure1 shows the geometry of two-dimensional parallel–plates electrochemical reactor electrodes in a multi-ion electrolyte solution including a copper deposition from 0.3 M $CuSO_4$ + 1 M H_2SO_4 electrolyte solution. Assuming complete dissociation as in [29], an ion-transport problem involving three ion species (Cu^{2+}, HSO_4^-, H^+) is solved. The computational domain is discretized into 162x82 uniform mesh. The advantage of numerical examples shown in Figure1 boundary conditions including a Butler-Volmer formulation is demonstrated for an electrolyte cell with parallel electrodes. The ionic properties of the solutions, containing three species is given in Table

1. These data are taken from Chung [8]. Sudden expansion case is considered for steady turbulent flow.
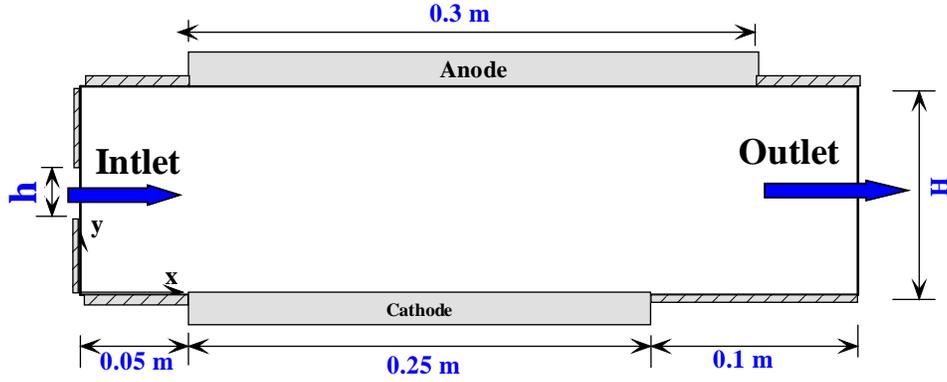

Figure 1. Sudden expansion with parallel electrode electrochemical reactor

TABLE 1: PHYSICAL PROPERTIES AND MODEL PARAMETERS

Case:steady , turbulent (3 species)
Electrolyte solution[8,29] 0.3 M $CuSO_4$ + 1 M H_2SO_4
C_{1ref} [mol/m^3]300
C_{2ref} [mol/m^3] 1300
C_{3ref} [mol/m^3]700
Z_1 [-]+2
Z_2[-] -1
Z_3[-] +1
D_1[m^2/s]0.61x10^{-9}
D_2[m^2/s]1.065x10^{-9}
D_3[m^2/s]9.312x10^{-9}
ρ [kg/m^3] 1020
μ [Pa.s]1.105x10^{-3}
T[K]298
Applied potential [volt] 0.6
Properties required for Butler-Volmer BC [29]
J_0[A/m^2] 25
γ [-]0.75
α_a 0.5
α_c 0.25

4. Numerical method

The average transport equations for mass and momentum of flow as well as for the turbulence in flow can be written for unsteady, incompressible, two-dimensional flows in the following general transport equation form:

$$\frac{\partial ...\{}{\partial t} + \nabla.(...u\{) = -\nabla p + \nabla.\left[\Gamma_{\{}\nabla\{\right] + S_{\{}} \qquad (1)$$

Where the variable $\{$ is the dependent variable, representing the streamwise velocity u, the normal velocity v, the turbulence kinetic energy k, dissipation rate v, the ionic concentration C_i and

potential volt ϕ, respectively. The diffusion coefficient $\Gamma_\{$ and source term $S_\{$ in the respective governing equation are specific to a particular meaning of φ, see Table 2. The numerical method employed here to solve the above general differential equation is based on a general method for prediction of heat and mass transfer, fluid flow and related processes. This method has been developed and proved its generality and capability in a wide range of possible applications for predicting physically meaningful solutions even for uniform grid by Patanker, SV. [31]. The control volume integration of the above general differential equation yields a discretized form being solved numerically on a staggered grid system. The governing equations are discretized using the hybrid scheme to achieve the best accuracy. In the present work, the SIMPLE algorithm of parameter is employed. The algorithm is started with the solution of the discretized momentum equations according to the associated boundary and initial conditions.

TABLE 2: GOVERNING EQUATIONS OF ELECTROLYTE SOLUTION

| Conservation of	$\{$	$\Gamma_\{$	$S_\{$
Mass	1	0.0	0.0
Axial momentum	u	u_{eff}	$-\dfrac{\partial p}{\partial x}+\dfrac{\partial}{\partial x}\left(\Gamma_{\sim eff}\left(\dfrac{\partial u}{\partial x}\right)\right)+\dfrac{\partial}{\partial y}\left(r_{\sim eff}\dfrac{\partial v}{\partial x}\right)$
Radial momentum	v	u_{eff}	$-\dfrac{\partial p}{\partial r}+\dfrac{\partial}{\partial x}\left(_{\sim eff}\dfrac{\partial u}{\partial y}\right)+\dfrac{\partial}{\partial r}\left(_{\sim eff}\left(\dfrac{\partial v}{\partial y}\right)\right)+g\,\text{S}..(C_i-C_{iref})$
Turbulent kinetic energy	k	$\dfrac{\sim_{eff}}{\dagger_k}$	$P-...\vee$
Dissipation rate	$\vee$	$\dfrac{\sim_{eff}}{\dagger_v}$	$\dfrac{\vee}{k}\left(C_{v1}P-C_{v2}...\vee\right)$
Species	C_i	$...D_i+\dfrac{\sim_t}{\dagger_t}$	$\dfrac{...Fz_iD_i}{RT}\nabla.(C_i\nabla\phi)$
Potential volt	ϕ	$|$	$\nabla.(\sum_i Fz_i(D_i+D_t)\nabla C_i)$

5. Results

In order to evaluate the quality of the simulation, computations have been performed on different important test cases with two-dimensional forms. Natural convection between two vertical electrodes (Cavity form) with supporting electrolyte of constant current density was the first test case, see [30]. The ability of the code to model turbulent mass transfer also, the turbulent flow in electrochemical reactor with parallel electrode (in a large duct and sudden expansion) was also considered. The extension of the code is devoted to the simulation of sudden expansion case in the present work.

5.1 Turbulent flow in a sudden expansion between parallel electrodes in a mult-ion electrolyte solution (electrodes with Butler-Volmer equation of current density)

A study to non-previous considered sudden expansion in a multi-ion electrolyte with parallel electrodes installed in the horizontal walls of the wide cross section is extended in this section. The geometry of such case is previously viewed in Figure 1. The standard $k-\varepsilon$ model is used to calculate the fluid dynamics in a sudden expansion parallel plate reactor with different

turbulent Schmidt number ($Sc_t = 1$ and 4.5). The Reynolds number based on the average inlet velocity and the height of the cell is 8333. Different aspect ratios of (AR=H/h) 1.0, 0.7, 0.5, 0.2 will be considered. The electrolyte consists of 0.3 M $CuSO_4$ + 1 M H_2SO_4, which is similar to case 1 (applied in the industrial range). The ionic properties of this electrolyte are given in Table 1; see Chung [8]. The resulting concentration and current density distributions for different turbulent Schmidt numbers with different area ratio of sudden expansion are shown in Figs. 2 and 3.
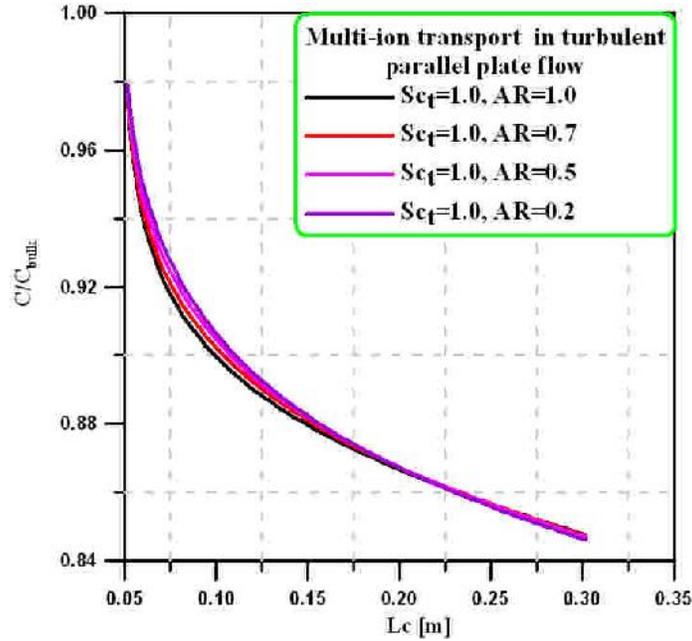
(a) $Sc_t=1.0$
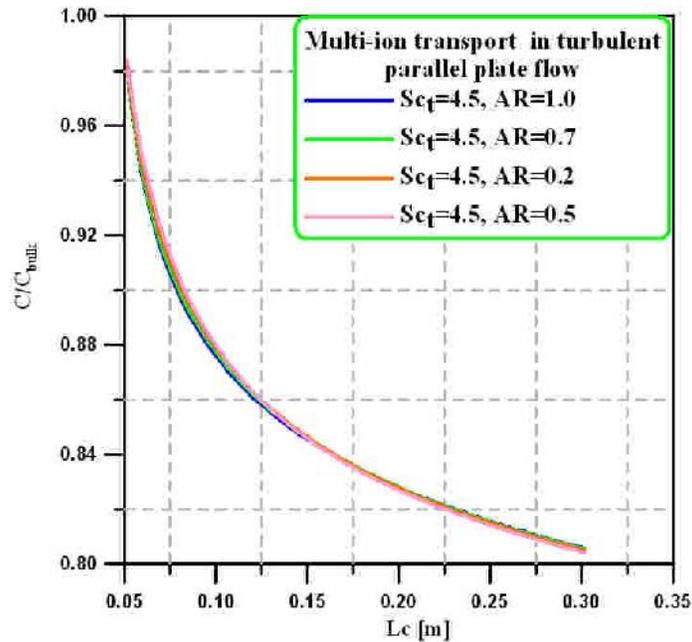
(b) $Sc_t=4.5$

Figure 2. Concentration of the Cu^{2+} ion distribution along the cathode for an imposed potential difference of 600 [mVolt], Re = 8333 and different area ratios, (a) $Sc_t=1.0$ and (b) $Sc_t=4.5$.
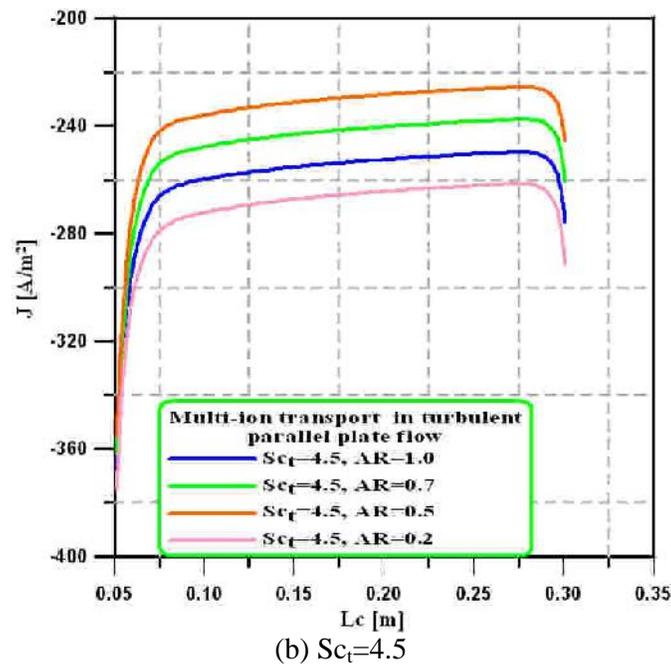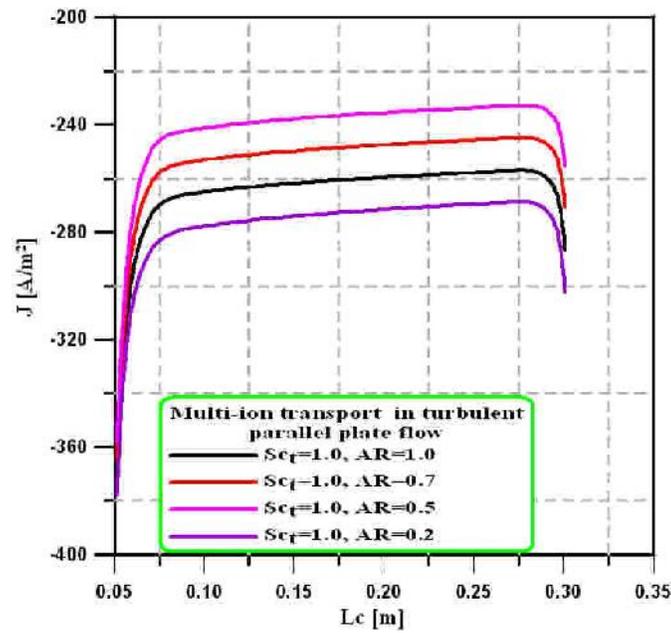
(a) $Sc_t=1.0$

(b) $Sc_t=4.5$

Figure 3. Current density for the Cu^{2+} ion along the cathode for an imposed potential difference of 600 [mVolt], Re = 8333 and different area ratios, (a) $Sc_t=1.0$ and (b) $Sc_t=4.5$.

As noticed, for constant Schmidt number, as the area ratio decreases this will leads to a small increasing the concentration on the cathode. This is not clearly observed in the case of the higher Schmidt number ($Sc_t=4.5$].
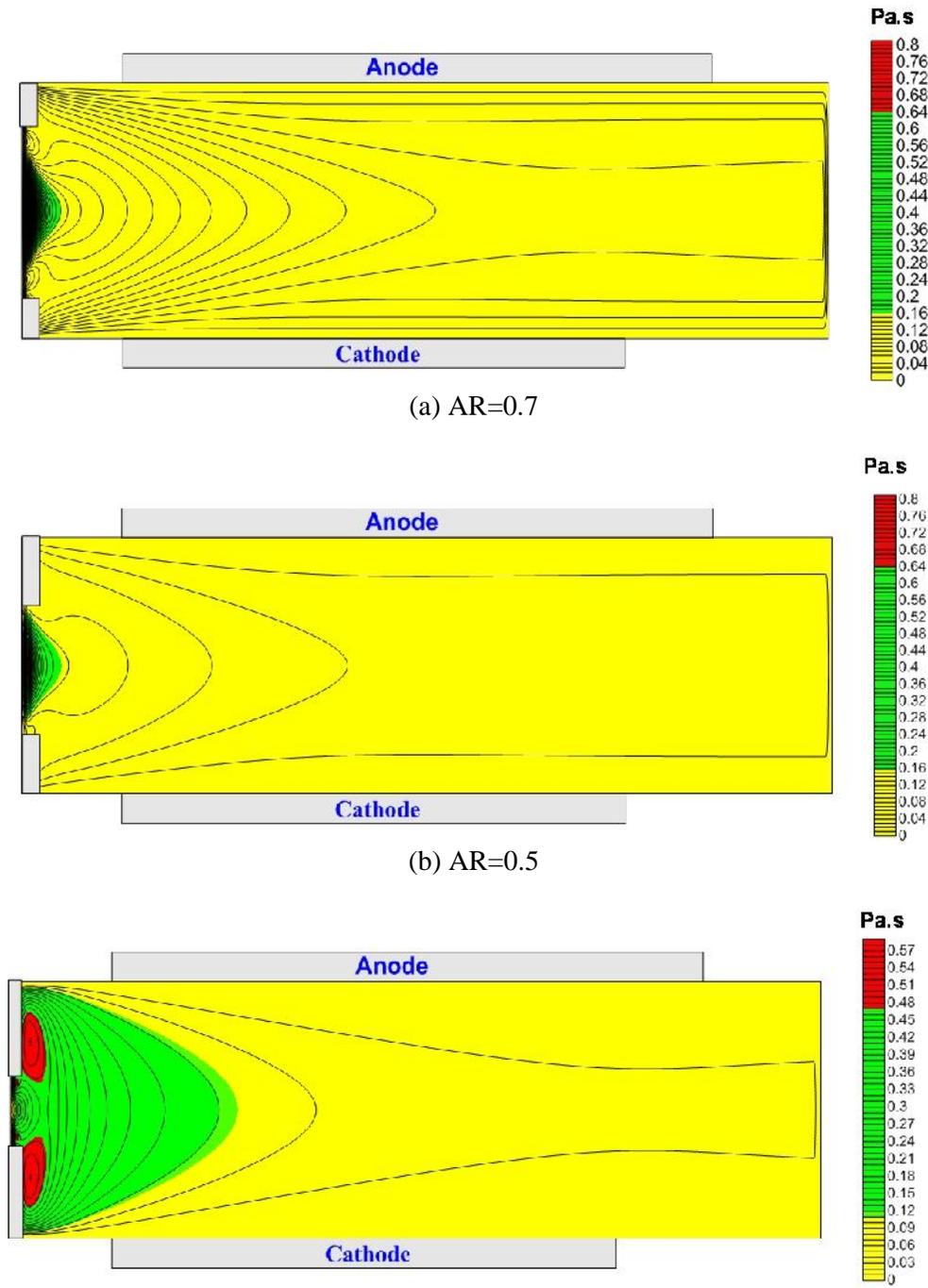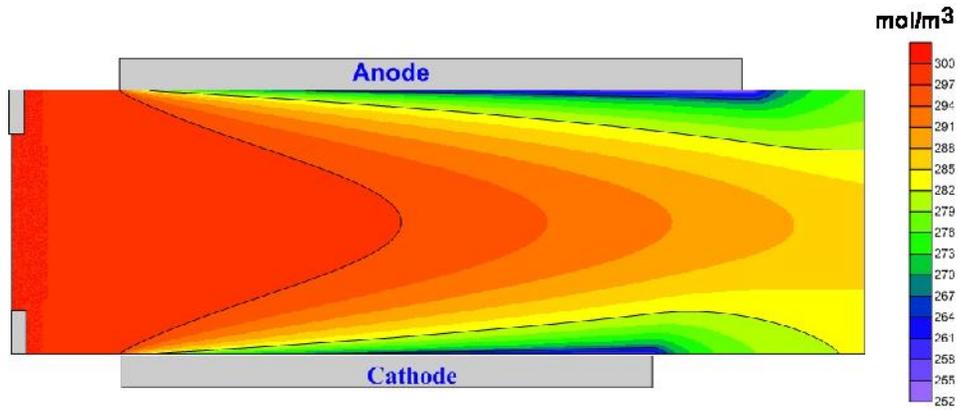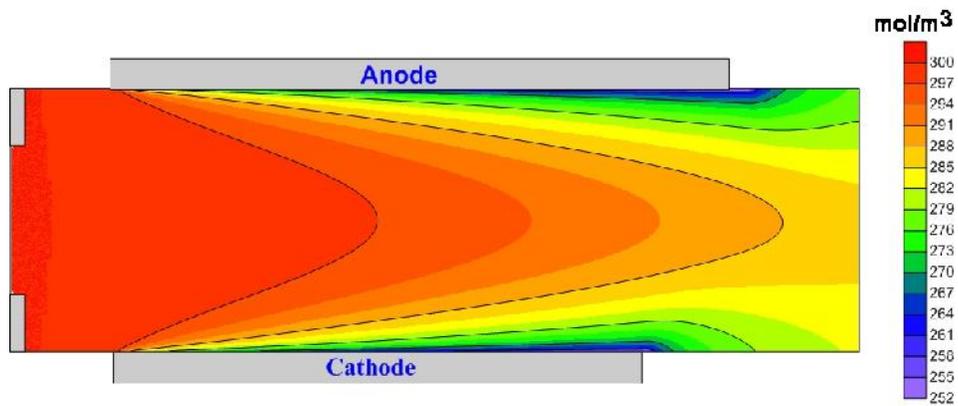
(a) AR=0.7

(b) AR=0.5

(a) AR=0.2

Figure 4. Turbulent viscosity of the Cu^{2+} ion for an imposed potential difference of 600 [mVolt], at Sc_t=1.0 and different area ratios (AR).

As discussed previously the higher turbulent Schmidt number cases an increase of the current density and hence a reduction of the concentration. The increase of turbulent viscosity with the small area ratio may be behind the explicit increase of concentration see Figure 4. Figure 5 presents the concentration contours at different area ratio for Schmidt number 1. As noticed, the reduction of area ratio accelerates the development of the concentration in the duct, because of the presence of high turbulence in this case

(a)AR=0.7

(b)AR=0.5
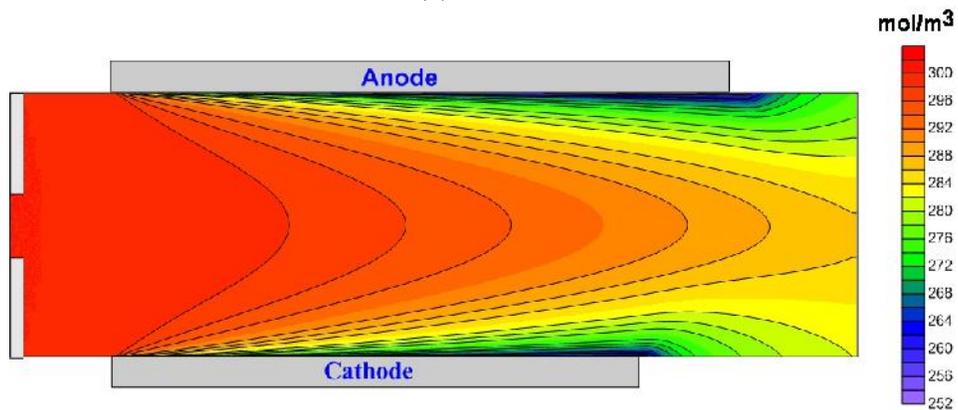

(c) AR=0.2

Figure 5. Concentration (mol/m^3) of the Cu^{2+} ion for an imposed potential difference of 600 [mVolt], at Sc_t=1.0 and different area ratios (AR).

Figure 6 shows the effect of area ratio in mass concentration boundary layer at different turbulent Schmidt number. It is observed the concentration boundary layer thickness increases with the decrease of area ratio in sudden expansion. The effect is small in the case of Schmidt number Sc_t=4.5. This explains what appears in Figs. 2 and 5.
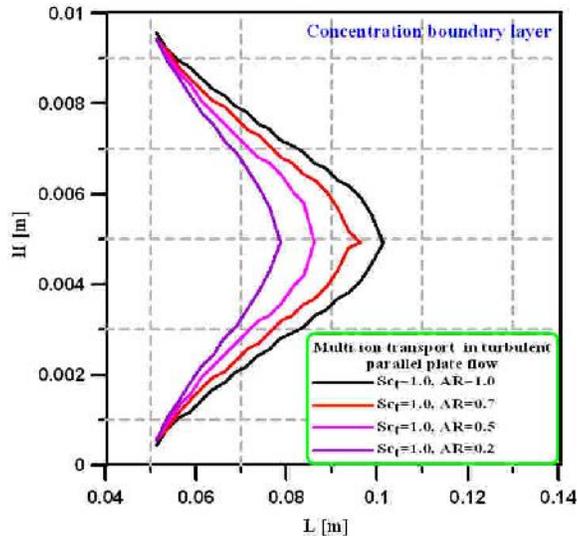
(a) Sc_t=1.0
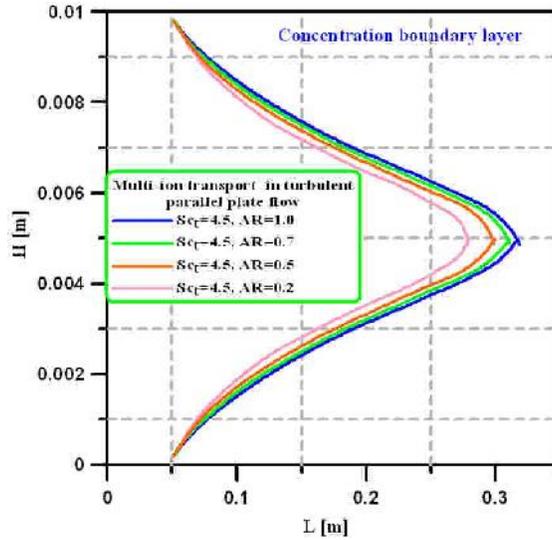
(b) Sc_t=4.5

Figure 6. Mass concentration boundary layer for an imposed potential difference of 600 [mVolt], Re = 8333 and different area ratios, (a) Sc_t=1.0 and (b) Sc_t=4.5.

6.   Conclusions

A computation of forced convection flows in a chemical solution inside a sudden expansion has been performed. The cathode and anode are installed in the widest parallel walls. The standard $k - v$ model has been chosen to simulate the turbulence behaviors. The results include the concentration, current density and the development of concentration boundary layer under different Schmidt numbers. The author extended the use of the code to simulate the flow dynamics and mass transfer in a sudden expansion geometry, in which. New results have been obtained, but the study needs a future experimental work that will be concerned. However, the present data encourage the present researchers to extent the code to study the two-phase flow dynamics in such geometries, one of the interesting studies in the field of Hydrogen production.

References

[1] J. Newman, K. E. Thomas-Alyea, Electrochemical Systems (3rd ed.), John Wiley & Sons, Inc., Hoboken; New Jersey, (2004).

[2] C. Wagner, The role of natural convection in electrolytic processes, J. Electrochem. Soc. 95 (1949) 161–173.

[3] J. R. Selman, J. Newman, Free-convection mass transfer with a supporting electrolyte, J. Electrochem. Soc. 118 (1971)1070–1078.

[4] Y. Awakura, Y. Takenaka, Y. Kondo, Studies on the velocity profile in natural convection during copper deposition at vertical cathodes, Electrochim. Acta 21 (1976) 789 – 797.

[5] Y. Fukunaka, K. Denpo, M. Iwata, K. Maruoka, Y. Kondo, Concentration profile of Cu2+ ion near a plane vertical cathode in electrolytes containing CuSO4 and an excess of H2SO4 as a supporting electrolyte, J. Electrochem. Soc. 130(1983) 2492–2499.

[6] Y. Awakura, E. Ebata, Y. Kondo, Distribution of local current densities during copper electrodeposition on a plane vertical cathode, J. Electrochem. Soc. 126 (1979) 23–30.

[7] X. Yang, K. Eckert, A. Heinze, M. Uhlemann, The concentration field during transient natural convection between vertical electrodes in a small-aspect-ratio cell, J. Electroanal. Chem. 613 (2008) 97–107.

[8] M. H. Chung, A numerical method for analysis of tertiary current distribution inunsteady natural convection multi-ion electrodeposition, Electrochim. Acta 45 (2000) 3959–3972

[9] C. F. Wallgren, F. H. Bark, R. Eriksson, D. S. Simonsson, J. Persson, R. I. Karlsson, Mass transport in a weakly stratified electrochemical cell, J. Appl. Electrochem. 26 (1996) 1235–1244.

[10] A. Ehrl, G. Bauer, V. Gravemeier, W.A. Wall, A computational approach for the simulation of natural convection in electrochemical cells, Journal of Computational Physics 235 (2013) 764–785

[11] Y.-K. Kwok, C.C.K. Wu, Fractional step algorithm for solving a multidimensional diffusion-migration equation, Numer. Methods Partial Differ. Equat. 11 (1995) 389–397.

[12] L. Bortels, J. Deconinck, B. Van den Bossche, The multi-dimensional upwinding method as a new simulation tool for the analysis of multi-ion electrolytes controlled by diffusion, convection and migration. Part 1. Steady state analysis of a parallel plane flow channel, J. Electroanal. Chem. 404 (1996) 15–26.

[13] M. Georgiadou, Finite-difference simulation of multi-ion electrochemical systems governed by diffusion,migration and convection, J. Electrochem.Soc. 144 (1997) 2732–2739.

[14] M. Georgiadou, Modeling current density distribution in electrochemical systems, Electrochim. Acta 48 (2003) 4089–4095.

[15] D. Barak-Shinar, M. Rosenfeld, S. Abboud, Numerical simulations of mass transfer processes in 3D model of electrochemical sensor, J. Electrochem. Soc.151 (2004) H261–H266

[16] M. Buoni, L. Petzold, An algorithm for simulation of electrochemical systems with surface-bulk coupling strategies, J. Comput. Phys. 229 (2010) 379–398.

[17] G. Bauer, V. Gravemeier, W.A. Wall, A 3D finite element approach for the couplednumerical Simulation of electrochemical systems and fluid flow,I.J.for numerical methods in engineering, 86 (2011) 1339–1359.

[18] G. Bauer, V. Gravemeier, W.A. Wall, A stabilized finite element method for the numerical simulation of multi-ion transport in electrochemical systems, Comput. Methods Appl. Mech. Engrg. 223–224 (2012) 199–210

[19] V.M. Volgin, O.V. Volgina, and A.D. Davydov, Finite difference method of simulation of non-steady-state ion transfer in electrochemical systems with allowance for migration,Computers and Chemistry, (000):1–12, 2000.

[20] V.M. Volgin, A.D. Davydov, Numerical Modeling of Non-Steady-State Ion Transfer in Electrochemical Systems with Allowance for Migration, Russ J. Electrochem. 31 (2001) 1197.

[21] R.H. Notter, A. Sleicher,The eddy diffusivity in turbulent boundary layer near awall,Chem. Eng. Sci. 26 (1971) 161.

[22] S.W. Churchill, A critique of the classical analogies for heat, mass, and momentum transfer, Ind. Eng. Chem. Res. 36 (1997) 3866.

[23] G. Nelissen, B. Van den Bossche, J. Deconinck, A. VanTheemsche, C. Dan, Laminar and turbulent mass transfer simulations in a parallel plate reacto, J. Appl. Electrochem. 33 (2003) 863.

[24] Y. Wang, J. Postlethwaite, THE APPLICATION OF LOW REYNOLDS NUMBER TURBULENCE MODEL TO CORROSION MODELLING IN THE MASS TRANSFER ENTRANCE REGION, Corros. Sci. 39 (1997) 1265.

[25] C. Rosen, C. Traegaardh, Prediction of turbulence high Schmidt number mass transfer using a low Reynolds numberturbulence model, Chem. Eng. J. 59 (1995) 153.

[26] F. Gurniki, K. Fukagata, S. Zahrai, F.H. Bark, Turbulent free convection in large electrochemical cells with a binary electrolyte, J. Appl.Electrochem. 29 (1999) 27.

[27] F.Gurniki, S.Zahrai, F.H.Bark, LES of turbulent channel flow of a binary electrolyte,J. Appl.Electrochem. 30 (2000) 1335.

[28] G. Nelissen, A. VanTheemsche ,C. Dan, B. Van den Bossche, J. Deconinck, Multi-iontransport and reaction simulations in turbulent parallel plate flow, Journal of Electroanalytical Chemistry 563 (2004) 213–220

[29] D. S. Ibrahim, C. Veerabahu, R. Palani, S. Devi, N. Balasubramanian, Flow dynamics and mass transfer studies in a tubular electrochemical reactor with a mesh Electrode, Computers &Fluids 73 (2013) 97–103.

[30] I.M. Sakr, W. A. El-Askary, A. Balabel, K. Ibrahim, Numerical Study on natural and forcedconvection in Electrochemical cells, Submitted to CFD letter.

[31] Patankar, S.V. (1980): Numerical heat transfer and fluid flow. Hemisphere Pub.Washington, DC, 1980.