Numerical Simulation of Flow Electrolysers: Effect of Various Geometric Parameters

Pragati Shukla*, K.K.Singh, P.K.Gupta and S.K. Ghosh
Chemical Engineering Group, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA-400085
*Corresponding author: pragati@barc.gov.in

Abstract: The objective of this work is to develop an understanding of coupled phenomena of electrolysis and fluid flow in flow electrolysers having stationary electrodes and to study the effects of various geometrical changes. Two-dimensional numerical simulations have been carried out using COMSOL 3.5 a. Effects of three geometrical parameters: 1) inlet channel length, 2) offset between anode and cathode and 3) Length of anode on the performance of electroneutral bulk of flow electrolyser have been studied.

Keywords: *Nernst-Planck, electrolyser, electroneutral bulk, current density*

1. Introduction

Flow electrolysers find several applications in industry. They are used for production of metals and synthesis of chemicals, gases. Cleaning and preservation of old artifacts, electrolytic refining of metals, electrolytic winning of metals, alkaline water electrolysis, anodization, electrometallurgy, electroplating, electrolytic etching of metal surfaces are other industrial applications of flow electrolysers. Due to their several industrial applications it is important to develop a fundamental understanding of the working of flow electrolysers. This understanding will eventually lead to optimum and efficient designs. In flow electrolysers, an inlet channel is often provided [1,2]. A previous study reports that by providing an inlet channel, current performance of an electrolyser can be enhanced [2]. However, an electrolyser with long inlet channel may cause high pressure drop and would require larger space for installation. Hence the inlet channel length should be optimum. One of the objectives of the present study is to investigate the effect of this important geometric parameter on the performance of the electrolyser. At times the length of the anode and cathode may not be same and there may be an offset between the positions of the anode and cathode [3]. The present work therefore also investigates the effects of these possibilities on the performance of a flow electrolyser. The simulations reported in this study involve coupled solution of Navier Stokes (NS) and Nernst Planck (NP) equations as in a previous study it was found that assumption of uniform velocity field may not give correct current density for a given applied voltage [2].

It may also be noted that these simulation focus only on electroneutral bulk of electrolyser. Simulations reported here are single phase simulations and do not account for the effects of gas evolution due to electrolysis.

2. Computational approach

2.1 Geometries and electrode reactions

A typical geometry used in simulation is, shown in fig. 1. This comprises of a rectangular domain of electrode length a=50 cm and width b=10 cm. To see the effect of inlet channel length, additional channel before the electrodes has been provided as shown in fig. 1. For the base case l=0 cm has been used and then it is varied from 20% to 100% of the electrode length to see the effect of inlet channel length. In the geometry to see the effect of offset, anode length c=20 cm and inlet channel length l=0 cm have been used and in the geometries to study the effect of the length of the anode, anode length is varied from 10 cm to 50 cm keeping l=0 cm, and offset zero.

The electrolyte considered is NaCl in water and electrode reactions involves only two charged species. Anode and cathode reactions are as follow

$2Cl^- \rightarrow Cl_2 \uparrow + 2e^-$ (Anodic reaction)

$Na^+ + e^- \rightarrow Na$ (Cathodic reaction)

The simulations are carried out for inlet velocity equal to 0.03 m/s and initial concentration of electrolyte equal to 600 mol/m^3.

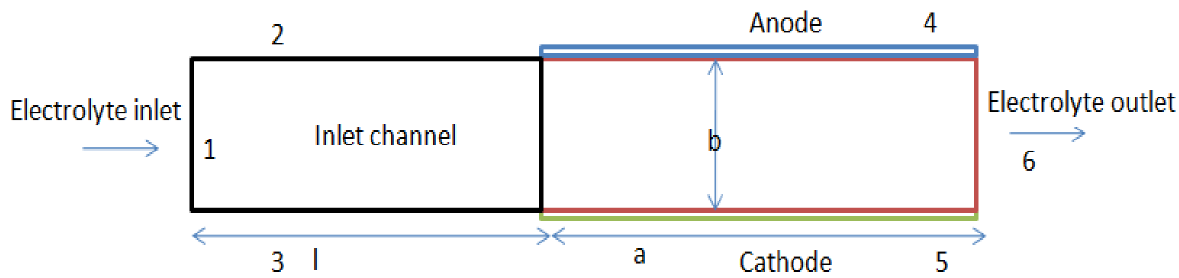

Figure 1. Geometry used for simulations

2.2 Governing equations

Incompressible, laminar and steady state electrolyte flow is considered. Applicable Navier- Stokes equations for continuity and momentum balance are as follow

$$\nabla \bullet \mathbf{u} = 0 \qquad (1)$$

$$\rho \mathbf{u} \bullet \nabla \mathbf{u} = \mu \nabla^2 \mathbf{u} - \nabla p + \rho \mathbf{g} \qquad (2)$$

Electrolyte solution consists of ions and when it is subjected to an electric field, transport of ions occurs by three mechanisms- migration, convection and diffusion: Migration because of potential gradient, convection because of bulk flow and diffusion because of concentration gradient. Nernst-Planck equation, mentioned below, accounts for all three type of transports and gives the total flux of the ionic species *i* in the solution.

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{mi} F c_i \nabla V + c_i \mathbf{u} \qquad (3)$$

Where c_i denotes the concentration, D_i is the diffusion coefficient, **u** is the velocity vector, F is Faraday's constant, V denotes electrical potential field, z_i is the charge number of the ionic species, and u_{mi} is the ionic mobility. Ionic mobility is related to diffusion coefficient and temperature as follows

$$u_{mi} = D_i \frac{F}{RT} \qquad (4)$$

Under steady state if there is no chemical reaction in electrolyte solution, following is applied

$$\nabla \bullet \mathbf{N}_i = \nabla \bullet (-D_i \nabla c_i - z_i u_{mi} F c_i \nabla V + c_i \mathbf{u}) = 0 \qquad (5)$$

Velocity field used in Eq. (5) is obtained from the solution of Navier-Stokes equations and that is how the two sets of equations are coupled with each other. The coupling is however one way with solution of Navier-Stokes equations affecting the solution of Nernst-Planck equation but solution of Nernst-Planck equation not affecting solution of the Navier-Stokes equations. Eq. (5) provides an equation for c_i. If there are n charged species, n-1 such equations are solved along with the following equation for the electroneutrality condition

$$\sum z_i c_i = 0 \qquad (6)$$

Solution of the above set of equations yields velocity, pressure, concentration of each species in the computational domain. Once the concentration field is available current density can be calculated using the following expression

$$\mathbf{i} = F \sum_{i=1}^{n} z_i (-D_i \bullet \nabla c_i - z_i u_{mi} F c_i \nabla V) \qquad (7)$$

It may be noted that in the above equation for current density there is no convective term owing to electoneutrality condition. It does not mean that the velocity field does not affect the current density. It affects current density by affecting the concentration field. In this study, a commercial code COMSOL Multiphysics 3.5 has been used to carry out the simulations.

2.3 Boundary conditions

Parameters used in the simulations are given in Table 1. The boundary conditions for the Navier-Stokes and Nernst-Planck modes for the geometry shown in fig.1 are given in Table 2 and 3, respectively.

Table 1: Different parameters used in the simulation

Species	Na^+ (species 1)	Cl^- (species 2)
D (x$10^{-9}m^2/s$)	1.33	2.03
c_0 (mole/m^3)	600	600

Table2: Boundary conditions for Navier-Stokes equations

Boundary	Type	Equation
1	normal velocity inlet	$\mathbf{u} = u_o$
2	no slip wall	$\mathbf{u} = 0$
3	no slip wall	$\mathbf{u} = 0$
4	no slip wall	$\mathbf{u} = 0$
5	no slip wall	$\mathbf{u} = 0$
6	pressure outlet with no viscous stress	$\mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)\mathbf{n} = 0 \quad p = p_o$

Table3: Boundary conditions for Nernst-Planck equations

Bd.	Current/Potential		c_2	
	Type	Eqn.	Type	Eqn.
1	Insulation	$\mathbf{n} \bullet \mathbf{i} = 0$	concentration	$c_2 = c_o$
2	Insulation	$\mathbf{n} \bullet \mathbf{i} = 0$	zero flux	$-\mathbf{n} \bullet \mathbf{N}_2 = 0$
3	Insulation	$\mathbf{n} \bullet \mathbf{i} = 0$	zero flux	$-\mathbf{n} \bullet \mathbf{N}_2 = 0$
4	Current density	$\mathbf{i} = i_o$	Faraday's law	$-\mathbf{n} \bullet \mathbf{N}_2 = \pm\frac{i_0}{F}$
5	Voltage	$V = V_o$	zero flux	$-\mathbf{n} \bullet \mathbf{N}_2 = 0$
6	Insulation	$\mathbf{n} \bullet \mathbf{i} = 0$	Convective flux	$-\mathbf{n} \bullet (-D_2\nabla c_2 - z_2 u_{mi2} F c_2 \nabla V) = 0$

2.4 Validation

Before proceeding to study the effect of geometric parameter on the performance of electroneutal bulk, the computational approach was validated by simulating a geometry reported in literature and comparing the predicted data with reported data [1]. Details of numerical simulations carried out to validate the computational approach are reported elsewhere and are omitted here for brevity [2].

Grid densities used in the present simulation are also based on the grid independence tests reported in an earlier study [2]. Fig. 2 shows the comparison of predicted result and reported result for one of the cases.

3. Effect of various geometrical parameters

3.1 Effect of inlet channel length

To see the effect of length of inlet channel, simulations have been carried out for different lengths of inlet channel ranging from 20% to 100% of electrolyser length. The results of simulations for current density range 2000 A/m^2 to 10,000 A/m^2 are shown in Fig. 3. The results indicate that performance of electroneutral bulk does improve by providing an inlet channel as potential difference across the electrodes for a given current density falls when l >0. However as inlet channel length is increased thereafter it eventually becomes constant. The results thus indicate that providing an inlet channel will be beneficial but not beyond a point. Pressure drop however will keep on increasing with increasing length of channel so the inlet channel length should be kept optimum. This kind of multiphysics simulations can help one identify this optimum inlet channel length. Fig. 3 also shows that it is important to consider both Nernst-Planck and Navier-Stokes equations while simulating flow electrolysers as predicted potential difference for the coupled solution is different from the solution in which only NP equation is involved.

3.2 Effect of offset between anode and cathode

To see the effect of offset between the anode and cathode a geometry in which anode length was 20 cm and cathode length was 50 cm, was considered. There was no inlet channel present for these geometries. Fig. 4 shows the effect of the offset between the anode and cathode on the potential difference across the electrodes. As expected, as the offset increases the potential difference across the electrode increases for a given current density. It is therefore better to design an electolyser in which anode and cathode are of different length such that the offset between the anode and cathode is kept minimum.

3.3 Effect of size of anode

Fig. 5 shows the effect of anode length on the potential difference across the electrodes for a constant total current. For these simulations also inlet channel was not considered. The offset between the anode and cathode is zero for these simulations. Fig. 5 shows that as the length of anode reduces the potential difference between the electrode increases. Fig. 6 show the vector plots of current density and surface plots of potential normalized with minimum value. For cases when anode length is 50 cm and 10cm. As can be seen when anode length is small area available for current to flow is smaller. This causes effective resistance between anode and cathode to increase leading to increase in potential difference across electrodes to increase for a given current as shown in fig. 5.

4. Conclusions

The simulations reported in this work provide useful insights into how the performance of a flow electrolyser is affected when certain geometric parameters namely inlet channel length, offset between anode and cathode and the length of anode are changed. Results show that providing offset, increases the potential drop for same applied current and hence leads to inefficient electroneutral bulk. The results also show that providing an inlet channel having length about 20-30% of electrode length improves the performance of electroneutral bulk. Simulations also show that as length of one of the electrode reduces keeping current same, performance of electroneutral bulk degrades. These multiphysics simulations also highlight that it is important to consider both Nernst Planck and Navier Stokes equations while simulating electroneutral bulk of a flow electrolyser.

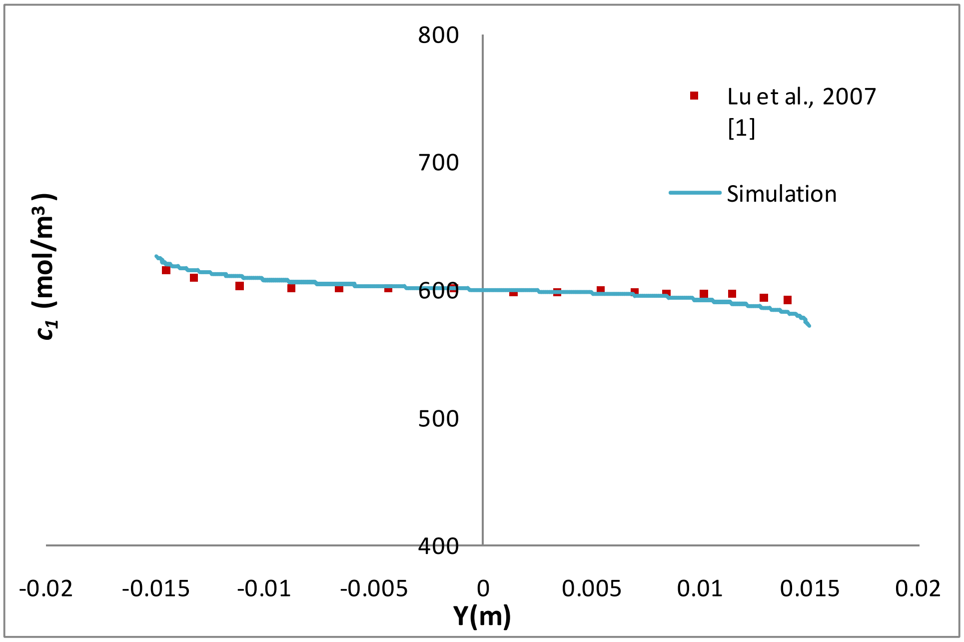

Figure 2. Concentration profile of species 1 at the outlet for $u_o = 0.05$ m/s, $i_o = 10000$ A/m^2, $c_o = 600$ mol/m^3

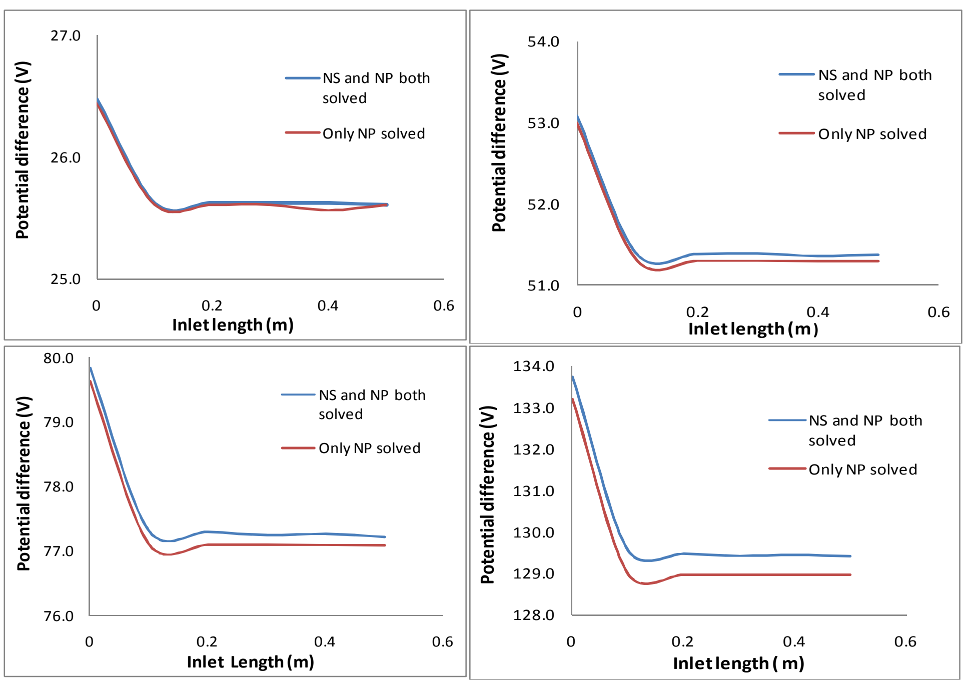

Figure 3. Effect of varying inlet channel length for current densities 2000, 4000, 6000 and 10,000A/m^2

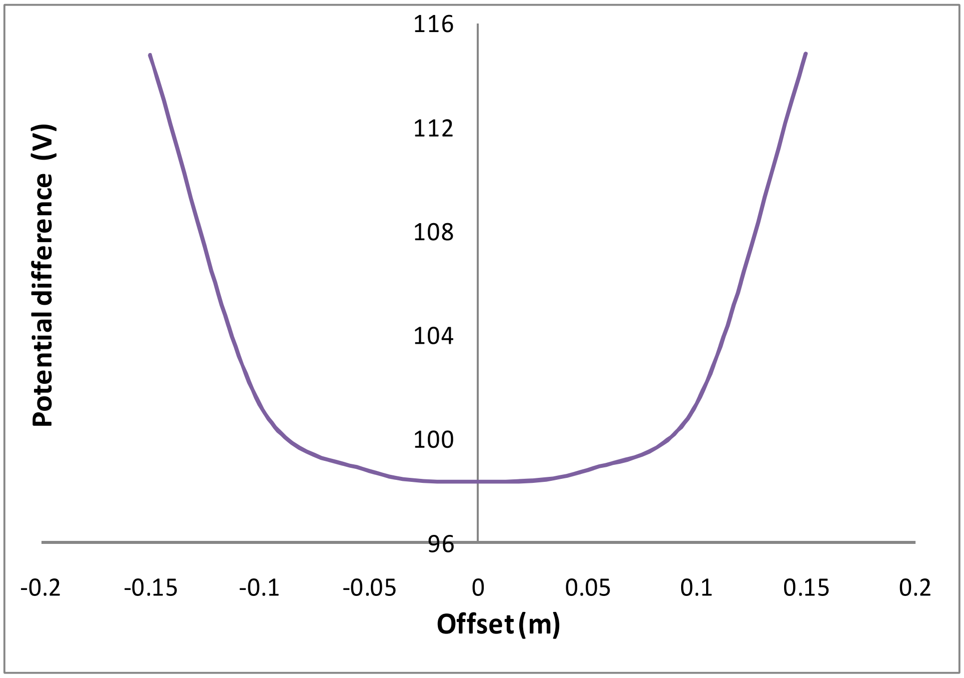

Figure 4. Effect of providing offset between the location of anode and cathode at current density 10,000 A/m^2

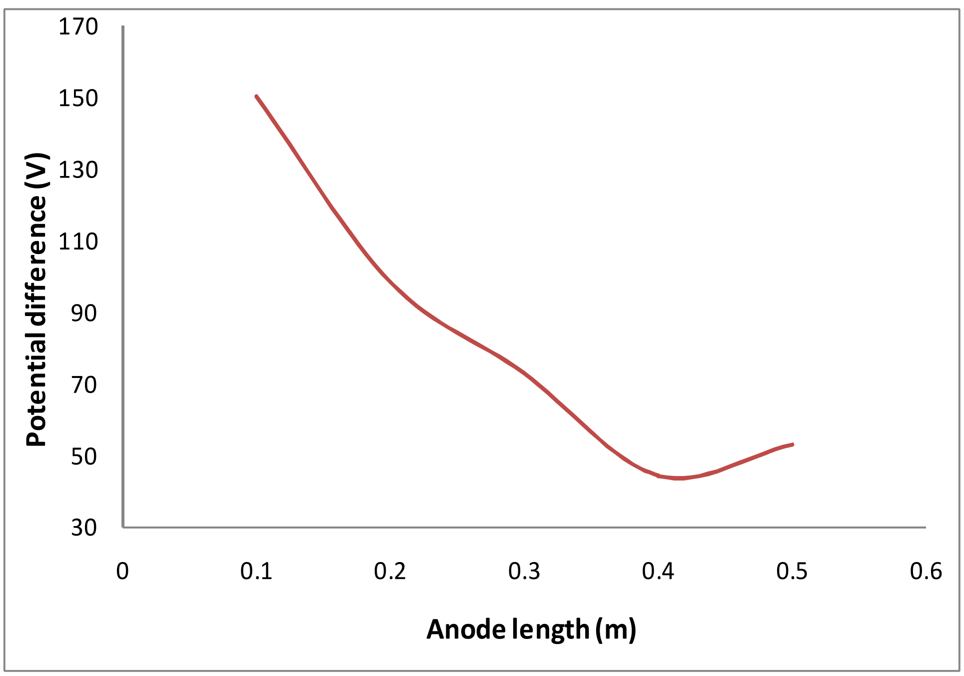

Figure 5. Effect of varying anode length on potential difference at current at current 2000 A

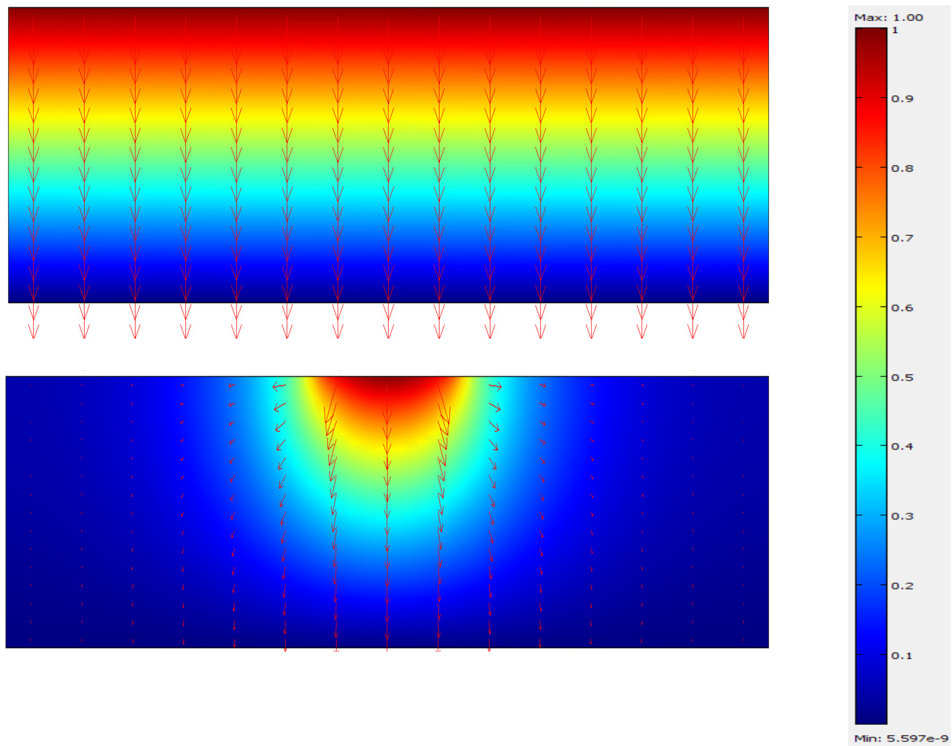

Figure 6. Surface normalized potential and current density vector plots for anodes of 10cm and 50 cm lengths at current 2000 A

5. References

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Notations

c_i Concentration of i^{th} species [mol m^{-3}]

c_o Inlet concentration [mol m^{-3}]

D_i Diffusivity of i^{th} species [m^2 s^{-1}]

F Farady's constant [Amp s (gm eq)$^{-1}$]

$\boldsymbol{g}$ Gravity vector [m s^{-2}]

$\mathbf{i}$ Current density vector [Amp m^{-2}]

$\mathbf{N}_i$ Flux vector for i^{th} species [mol m^{-2} s^{-1}]

p Pressure [kg m^{-1} s^{-2}]

R Gas constant [Kg mol^{-1} m s^{-2}K^{-1}]

T Temperature [K]

$\mathbf{u}$ Velocity vector [m s^{-1}]

u_{mi} Ionic mobility [Kg^{-1} m s^{2}Amp]

V Voltage or potential [Volts]

z_i Charge number of i^{th} species [-]

Greek Symbols

μ Viscosity [kg m^{-1} s^{-1}]

ρ Density [kg m^{-3}]