Chemical Engineering Science 66 (2011) 2252–2260

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Liquid–gas flow patterns in a narrow electrochemical channel

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ARTICLE INFO

Article history:
Received 9 September 2010
Received in revised form
12 February 2011
Accepted 23 February 2011
Available online 1 March 2011

Keywords:
Bubble
Electrochemistry
Fluid mechanics
Laminar flow
Mathematical modeling
Multiphase flow

ABSTRACT

The flow in a narrow (3 mm wide) vertical gap of an electrochemical cell with gas evolution at one electrode is modeled by means of the two-phase Euler–Euler model. The results indicate that at certain conditions an unsteady type of flow with vortices and recirculation regions can occur. Such flow pattern has been observed experimentally, but not reported in previous modeling studies. Further analysis establishes that the presence of a sufficient amount of small ($\sim$10 μm) bubbles is the main factor causing this type of flow at high current densities.

1. Introduction

Electrochemical cells with gas evolution at one or both electrodes are commonly used. The gas in the electrode gap (channel) affects the liquid flow distribution and ionic transport to the electrode surfaces, which can have a considerable effect on cell performance. Thus, a number of studies of various degrees of complexity appeared in the literature dedicated to the modeling of gas-evolving electrochemical cells (see Vogt, 1983 for a review). In many of these studies a simplified steady state liquid velocity profile in the cell is assumed *a priori* in order to close the set of equations that describe the mass balance of the various species. None have addressed the issue of gas–liquid flow regime in the channel. Recent experiments (Boissonneau and Byrne, 2000; Hell and Wanngard, 2009), however, indicate that the two-phase flow pattern in the channel can be much more complex than previously assumed and, in particular, that stationary vortices and recirculation cells can emerge in the flow. Up to now, however, all studies (e.g. Wetind and Dahlkild, 2001; Aldas et al., 2008; Mat and Aldas, 2005; Mat et al., 2000) that specifically focused on CFD modeling of the flow in electrochemical channels with gas evolution did not report the flow pattern observed in these experiments. We attribute this to two factors. In some cases (Aldas et al., 2008; Mat and Aldas, 2005; Mat et al., 2000) only relatively large bubbles ($\sim$0.1 mm) are considered in the models. In other studies (Wetind and Dahlkild, 2001) that take into consideration the effect of the small bubbles, the flow modeling is limited to steady state calculations.

The aim of this study is to test the transient Euler–Euler model for computing gas–liquid flow patterns in these channels. The model should be capable of determining whether complex flow patterns, suggested by experiments, can be numerically observed and should provide the means for estimation of conditions that lead to the flow regime transition. This is important for proper execution and interpretation of cell performance experiments and models which must incorporate the correct flow field.

We examine first the phenomena affecting gas–liquid in a single narrow vertical channel in which only one wall is a gas producing electrode (see Fig. 1). Based on physical considerations one can conclude that the two-phase flow pattern in the channel is entirely induced by the gas generated along the vertical electrode surface. The gas holdup profile develops in the direction perpendicular to the electrode and this drives the vertical liquid motion by buoyancy force gradients. In this buoyancy driven flow, at low gas production rates at the electrode, one expects the liquid (in the batch system considered here) to re-circulate gently, most likely in a single elongated cell, since it cannot leave the

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doi:10.1016/j.ces.2011.02.046

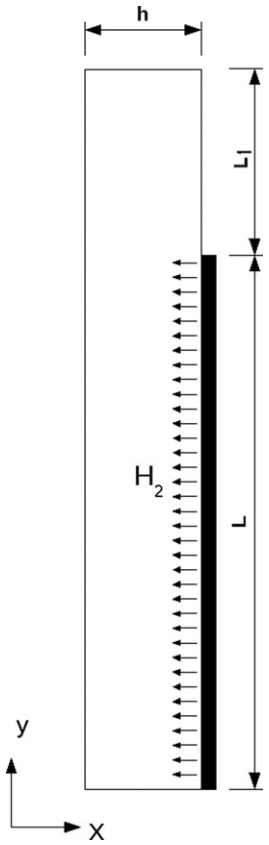

Fig. 1. The single channel geometry used in the simulations (figure not in scale).

channel. The flow is stationary and at quasi-steady state. One intuitively expects that at high enough gas production rate this quasi-steady flow pattern will break down. This transition should occur earlier at higher average gas holdup in the channel, as increased presence of the gas limits the ability of the liquid to complete a single circulation cell which is expected at lower gas injection rates. At given gas injection rate smaller gas bubbles lead to higher average gas holdup due to the fact that their relative velocity is much smaller than that of large bubbles.

We expect a model based on basic principles of fluid dynamics to be able to capture the trends anticipated above and for which some experimental evidence exists (e.g. emergence of unsteady flow patterns). Since the detailed physics of the gas generation at the electrode surface, bubble coalescence, and gas disengagement at a free surface in electrolyte solutions are not completely understood, direct numerical simulation is not an option. We chose the unsteady state Euler–Euler model because we have had considerable success with it in describing buoyancy driven flows in bubble columns (Pan et al., 2000; Chen et al., 2005; Rafique et al., 2004). This model is also preferred in industrial practice when all scales of the physics of the system are not precisely known. Moreover, the implementation of the model is readily available in a number of commercial codes such as FLUENT, CFX and other. We chose Open Source Field Operation and Manipulation (OpenFOAM) (OpenCFD, 2010; Weller et al., 1998) because the source code is available in the public domain and can therefore be extended to include electrochemical reactor performance. Using this model, our goal is to determine whether one can numerically detect different flow patterns as a function of gas flux at the electrode and whether one can capture the transition from quasi-steady to oscillatory patterns with multiple recirculation cells observed in some experiments. Our goal is also to test our hypothesis that at fixed gas flux at the electrode only a number of sufficiently small bubbles can give rise to these pseudo-turbulent flows. This is very valuable information that currently is not available.

2. The electrochemical channel

As already stated, here we consider only a batch electrochemical cell that contains a confined finite volume of liquid and has a single gas evolving electrode. Fig. 1 displays the geometrical configuration of interest which is used in our simulation. The bottom of the channel is a solid wall and the top corresponds to the liquid free surface. The anode (where no gas is generated) is located at $x=0$. The cathode, where gas bubbles are generated, is at $x=h$; L is the length of the solid cathode. The additional inert wall segment L_1 above the gas-producing section is often used in both experimental devices (Boissonneau and Byrne, 2000) and numerical investigations (Wetind and Dahlkild, 2001) and we employ it here as it stabilizes the computations. The value of channel width h is 3 mm, which is common for industrial applications like chlorate, hypochlorite or perchlorate cells. The length L is variable ($L=30$, 60 or 90 mm), while L_1 is fixed at 20 mm for the results presented here (the choice of this value is explained in Section 4.4). As already mentioned, it is assumed that the anode does not produce gas. This is also reasonable in chlorate, hypochlorite or perchlorate cells, where the Cl_2 produced at the anode remains in solution by reacting immediately with water and does not evolve as gas. Oxygen or any other gas production at the anode is ignored. The physical properties of the liquid are assumed to be those of water ($\mu_\ell=8.9\times10^{-4}$ kg m^{-1} s^{-1}, $\rho_\ell=997$ kg m^{-3}), while the gas generated at the cathode is H_2 ($\mu_g=8.76\times10^{-6}$ kg m^{-1} s^{-1}, $\rho_g=0.07$ kg m^{-3}). The density and the viscosity of concentrated aqueous solutions of electrolytes can be larger than pure water, but for the moment, this is not taken into account.

The rate of gas production at the cathode (i.e. the wall in Fig. 1 at $x=h$) follows the Faraday law and the gas flux at the electrode surface is related to the employed current density by

$$j_{gas}=\frac{iM}{zF\rho_g}, \tag{1}$$

where $z=2$ is the number of electrons involved in the electrochemical reaction ($2H_2O+2e^-\rightarrow H_2+2OH^-$), $M=2\times10^{-3}$ kg mol^{-1} is the molecular mass of H_2, i the current density and $F=96{,}487$ A s mol^{-1} the Faraday constant. In this paper, we focus only on the flow field and thus we assume that the current density is known so that the gas flux at the cathode is given by Eq. (1).

3. Flow equations

Our model of the two-phase flow in the channel of Fig. 1 is subject to the following assumptions:

(a) The continuous phase is incompressible and Newtonian.
(b) The flow field is two-dimensional, since the third dimension (other width) of the channel is two–three orders of magnitude larger than the distance h.
(c) Temperature and all the physical properties of the channel material and fluid are constant.
(d) The bubbles can be treated as rigid particles, since the diameter of the bubbles is small (Boissonneau and Byrne, 2000).
(e) Turbulence is not considered. Reynolds number is very low since both the gas–liquid relative velocity and the bubble diameter are very small. The bubble Reynolds number is the