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Strongly coupled model for the prediction of the performances of an electrochemical reactor

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HIGHLIGHTS

- Through this model, a wider range of electrochemical systems can be investigated.
- Buttler-Volmer, linear and Tafel forms can be applied accordingly to the needs.
- Current density distribution is correctly predicted along the active plates.
- Deformations of the electrodes due to material deposition and corrosion are modeled.
- Results can optimize the performances of electrolytic cells on industrial scales.

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ABSTRACT

A mathematical model is developed to investigate and predict the performances of electrochemical reactors. It is implemented with a finite volume method, and solved by means of the open source package OpenFOAM. The new solver, named *ECpisoFOAM*, deals with an intricate set of equations and boundary conditions which describe an electrochemical copper deposition system. The code uses the PISO algorithm for the transient incompressible flow field. A second predictor-corrector sequence combines mass fraction, electric potential and current density. It considers the convection, migration and diffusion mechanisms under the assumption of a dilute solution, mass conservation, and local electro-neutrality. The conservation of charges provides the electrical field which in turn allows the reconstruction of the tertiary current density distribution. At the electrodes, the presence of a charged double layer affects the behavior of the neighbor electrolyte. The effect of this interaction is modeled through the Butler-Volmer equation or its two commonly used simplifications: linear and logarithmic. Furthermore the fluid dynamic and the electrochemical modeling are coupled with the geometric changes of the active plates due to either material deposition or consumption of the electrodes. A dynamic mesh method has been integrated, increasing yet the level of coupling between electrical, chemical and fluid dynamic fields. Results are here presented and analyzed.

1. Introduction

Electrochemical reactors and in general electrochemical systems nowadays, have a leading role in a wide range of applications: from batteries to fuel cells, from electroplating to water treatments. The main physical characteristic of an electrochemical system, as viewed through the eyes of engineers and scientists, is indeed the simultaneous treatment of many complex and interacting phenomena (Newman and Thomasn-Alyea, 2004; Bard and Faulkner, 2001). To overcome the issue, several simplifications are commonly used with the intent to decrease the level of coupling. They provide satisfactory estimation of the solution, but cut down the generality of the problem and restrict the solution's domain to very specific cases. Alternatively, commercial software use specific packages for electrochemical reactors, presenting "black-box" solutions that allow little insight into the mathematical and numerical difficulties of the model. Therefore, it is of interest for research engineers the need to operate with a tool having a penetrable architecture such as *OpenFOAM* (OF). This is a free, open source software package, specialized in Computational Fluid Dynamics (CFD) with a large user base across most areas of engineering and science, offering complete freedom to customize and

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Nomenclature

$asyR$	asymptotic range of convergence (–)
C_i	concentration of the i-th species (kg-mol m^{-3})
C_{TOT}	total electrolytic concentration (kg-mol m^{-3})
$\boldsymbol{d}$	point displacement vector field (m)
d_{imp}	imposed point displacement (m)
D_i	diffusivity of the i-th species (m^2 s^{-1})
E^0	standard electric potential (V)
E^0_{RE}	standard electric potential of the reference electrode (V)
E^∞	equilibrium potential (V)
F	Faraday's constant (A s Kg-mol^{-1})
Fs	security factor (–)
f	functional (m)
H	electrode's height (m)
$\boldsymbol{i}$	current density per units of C_{TOT} (A s Kg-mol^{-1})
i_0	exchange current density at null potential (A s Kg-mol^{-1})
$\boldsymbol{i}_k$	$\boldsymbol{i}$ of the k-th reaction per units of C_{TOT} (A s Kg-mol^{-1})
i_{lim}	limiting current density (A s Kg-mol^{-1})
k_m	mass transfer coefficient (m s^{-1})
L	electrode's length (m)
L_c	characteristic length (m)
l^2	squared distance from the moving node (m^2)
m	order of convergence of the solution (–)
$\boldsymbol{N}_i$	flux of the i-th species per units of C_{TOT} (m s^{-1})
n	number of electrons exchanged (–)
Pe	Peclet number (–)
p	pressure (Pa)
R	gas constant (J Kg-mol^{-1} K^{-1})
R_{ct}	charge transfer resistance (Ω Kg-mol m)
r	grid refinement ratio (–)
S	rate of homogeneous chemical reaction (s^{-1})
Sh	Sherwood number (–)
s_{ik}	stoichiometric coefficient of the i-th species (–)
T	bulk temperature (K)
t	time (s)
$\boldsymbol{U}$	velocity (m s^{-1})
$\boldsymbol{U}_{in}$	inlet velocity (m s^{-1})
V_{el}	measured electrode potential (V)
ΔV_{cell}	imposed cell voltage (V)
Y^b_i	bulk mass fraction of the i-th species (–)
Y_i	mass fraction of the i-th species (–)
$Y_{i,RE}$	Y_i at the reference electrode (–)
Y^b_{ox}	bulk mass fraction of the oxidant (–)
Y^s_{ox}	mass fraction of the oxidant at the plate (–)
Y^b_{red}	bulk mass fraction of the reductant (–)
Y^s_{red}	mass fraction of the reductant at the plate (–)
z_i	charge number of the i-th species (–)

Greek letters

α	symmetry factor (–)
η_{el}	electrode overpotential (V)
ν	kinematic viscosity (m^2 s^{-1})
Φ	electric potential (V)
Φ^s	surface electric potential (V)
ρ	solvent density (kg m^{-3})

extend its existing functionality. In this work the flexibility of OF is exploited to allow a more direct control over the performances of an electrochemical cell in terms of:

- uniform current density distribution
- uniform electrode potential distribution
- high mass transfer rates (Rivera et al., 2015)

An example of a typical electrochemical cell is the FM01-LC reactor. It is a scaled-down version of the FM21-SP cell (2.1 m^2) which is employed in the chloralkali production (technologies enterprise, 2016). Its design produces a controlled flow by means of a parallel plate cells, often in a modular, expandable, filter-press configuration (Walsh, 1993). Despite the fact that this technology is well-spread, fluid mechanics, turbulence and electro chemistry remain strongly coupled, hence the modeling of these systems is still today a very challenging task. For this reason the present work aims to set up, implement and develop a numerical model that can investigate and predict the productivity of an electrochemical reactor system.

2. Geometry and mesh

The above mentioned FM01-LC belongs to the family of the Parallel Plate Electrochemical Reactors (PPER). A PPER, is a vessel which facilitates chemical reactions through the introduction of electrical energy, where an anode and a cathode are assembled on parallel slabs (White et al., 1983). The electrodes are physically separated by an electrolyte medium containing reactants and products. The electrolyte is injected in the reactor with a certain known velocity, and it reacts with the active electrodes. Inside the cell two half-sides are identified. Species are oxidized in one half-cell (anode), while in the other half-cell (cathode) species are reduced.

In this work the parallel plate configuration is used as a test-case. The full cell is represented by a rectangular geometry. Table 1 provides its dimensions and the number of grid elements for both the active plates (read anode and cathode), and the not actives. It can be noticed that the flow is 2D (1 grid element in the y-direction), and it is discretized with a total number of 22,750 elements for the entire reactor. Fig. 1 shows a simplified sketch of it.

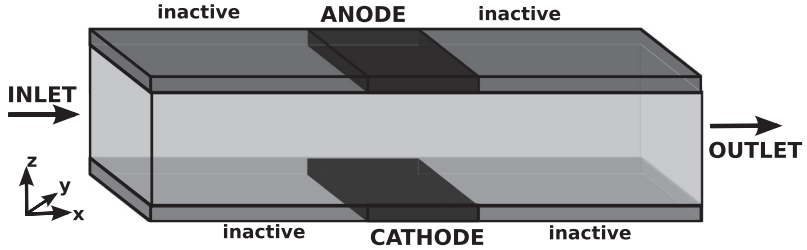

Fig. 1. Sketch of the geometry.