

Finite-element method simulation of rotating disk flow: effect of the transport of a chemical species

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Electrochemical cells containing an iron rotating disk electrode which is dissolved in the electrolyte, an 1 M H_2SO_4 solution present a current instability in the plateau region, where the current is controlled by the mass transport. Dissolution of the electrode gives rise to a thin concentration boundary layer, due to a Schmidt number $Sc = 2000$. This boundary layer, together with the potential applied to the electrode, leads to an increase in the fluid viscosity and in a decrease in the diffusion coefficient, coupling the concentration and the chemical species field. Since the current is proportional to the concentration gradient at the interface, an instability of the coupled fields at Reynolds numbers attained in experimental conditions could be responsible for the current instability. Mangiavacchi [1] performed a linear stability analysis of the problem and showed that this is indeed the case. In this paper we review the main results of the stability analysis and present the main features of the FEM code recently developed in our group, to proceed with the investigation of the current instability observed in electrochemical cells.

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1 Introduction

Electrochemical cells using a rotating disk electrode are a widely used experimental tool in electro chemistry, due to the simplicity of the setup and the fact that the mass flux, at steady state conditions, is independent of the radial position along the disk [2]. Polarization curves obtained in such cells present a *plateau*, where the limit current is proportional to the square root of the electrode angular velocity, being thus strongly affected by the hydrodynamics. We consider an electrochemical cell with an iron rotating disk electrode, which is dissolved in an 1 M H_2SO_4 electrolyte, as shown schematically in Fig. (1). Such cells present a current instability at the beginning of the *plateau*, which appears at a certain value of the applied potential and is suppressed beyond another value [3].

Dissolution of the electrode gives rise to a thin concentration boundary layer, due to a Schmidt number $Sc = 2000$. This boundary layer, together with the potential applied to the electrode, couples the hydrodynamic and concentration fields, through an increase in the fluid viscosity and a decrease in the diffusion coefficient. Since the current is proportional to the concentration gradient at the interface, an instability of the coupled fields at Reynolds numbers attained in experimental conditions could be responsible for the current instability.

2 Base state and linear stability analysis

Mangiavacchi [1] performed a linear stability analysis of the problem and showed that this is indeed the case. The base state is the modified von Kármán's solution for rotating disk flow, now coupled to the concentration field of a representative chemical species, through the dependence of the viscosity on the concentration. An exponential law is assumed, in the form $\nu = \nu_\infty \exp(mC)$, where ν_∞ is the bulk viscosity, m is obtained based on experimental electrochemical data and the non dimensional concentration C varies from 0 far from the electrode to 1 at the interface. The diffusion coefficient D is also affected by the concentration field, according to the Stokes-Einstein law, $D\nu = D_\infty\nu_\infty$. Barcia *et al.* showed that migration of ions due to the electrical field is negligible and that the current is thus, basically proportional to the concentration gradient at the interface: $i \propto (dC/dz)_{z=0}$. Therefore, since i depends on m , and i is known from the experiments, an iterative procedure is employed to find the value of m that matches the experimental data.

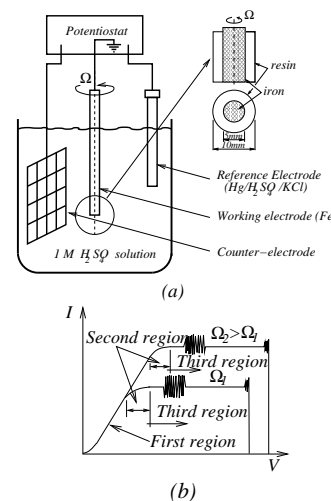


Fig. 1 The electrochemical with a rotating disk electrode and a scheme of typical polarization curves obtained in such cells.

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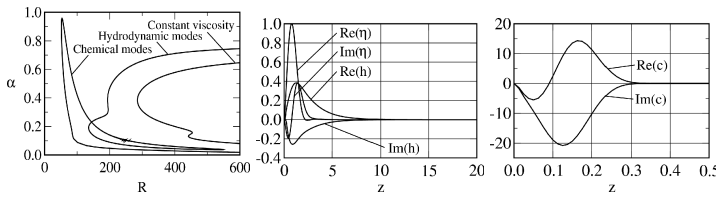


Fig. 2 Neutral curve for constant and for variable viscosity fluids (left), in the $\alpha \times R$ plane, where R is the non-dimensional radius or Reynolds number. Hydrodynamic eigenmode and concentration eigenmodes associated to a point in the inner unstable region are shown on the center and right panels.

verse power method in a grid of uniformly spaced points. We have considered perturbations turning with the angular velocity of the electrode only. The eigenfunctions of the problem depend on the axial coordinate and contain the vertical component of the velocity h , the vertical component of the vorticity η and the concentration c . The results show the existence of a new unstable region at Reynolds number on the range of typical experimental conditions. Rates of growth of modes in this region are more than one order of magnitude smaller than in the region of hydrodynamic modes. However, the concentration component of the eigenmodes are one order of magnitude larger than the hydrodynamic variables and confined to a thin layer, 20 times thinner than the hydrodynamic layer. In consequence, $(dc/dz)_{z=0}$ attains values that seem large enough to produce detectable current oscillations.

3 FEM-DNS and results

The results of the linear analysis suggest that a direct numerical simulation of the problem could reveal even more interesting results. In this sense a FEM code has been developed, with the following characteristics: pressure and diffusive terms are treated by a Galerkin method, convective terms are treated in a semi-lagrangian form in order to assure the necessary stability to the code. Time is discretized according to a first order forward differences scheme and the resulting linear systems are solved by a projection method. The application of the projection method decouples the velocity and pressure fields computations, resulting in two symmetric and positive definite matrices that are solved by the preconditioned conjugate gradient method. A reverse Cuthill-McKee reordering and an incomplete Cholesky preconditioning scheme are applied to solve the linear systems efficiently. Cubic tetrahedral elements are employed, with the velocity evaluated at the vertices and the centroid of the element. Pressure is evaluated at the vertices only (mini-element). Variables from the previous time step are used to evaluate the chemical species field, decoupling the hydrodynamics from the scalar variable transport.

Fig. 3 shows results of the FEM simulations: the velocity profiles for constant viscosity, first figure, and for variable viscosity, second figure. The results agree with the analytical von Kármán solution [4]. The boundary layer for the variable viscosity is thicker than the constant viscosity case, and presents an additional inflection point, increasing thus the instability of the profile.

The FEM code is now validated and will be employed for the simulation of the nonlinear evolution of the most unstable modes found in the linear analysis.

References

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A perturbation in the form $\mathbf{F} \exp(\alpha r + \beta \theta - \omega t) + cc$ is superposed to base state. Here, \mathbf{F} is a vector of functions containing the dependence of the three components of the velocity, the pressure and the concentration of the chemical species along the axial direction z . ω is a complex number, with the real part being the angular velocity of the perturbation and the imaginary part being the rate of growth. The perturbation is introduced in the linearized evolution equations, leading to an eigenvalue-eigenfunction problem, solved by the in-

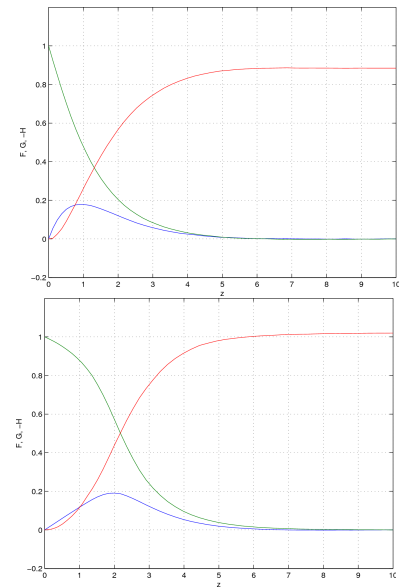


Fig. 3 Velocity profiles obtained from the FEM simulation of the disk flow for constant viscosity fluids (first) and stratified viscosity (second).