A SULFIDE-DRIVEN FUEL CELL:
THE CATHODE CELL WITH EJECTOR MIXER
Part 2. Double density mesh

The institute of Chemical Engineering in Sofia
Keywords

FC, ORR, CFD, visualization, velocity distribution, $\epsilon$-distribution related to mass transfer
($\epsilon$ = rate of energy dissipation rate)
Main topics

- Introduction
  - Driving force of the study
- Aim of this study
  - A global and a more specific one
- Cathode chamber design
- Methods CFD
  - Numerical model and procedure
- Results
  - Characteristics of the ejector cell
    - Overview of previous results *(refreshment)*
    - Framework of a further study
    - Mesh refinement results
- In conclusion
  - Further cell geometry
Introduction

Driving forces of the study

- There are just a few studies on the problem
- Development of a technical-scale process
Aims of the study

Global aim

Development of a technical-scale process

More specific aims

(1) To formulate a flow model of the cathode cell and

(2) To characterize the flow field in view of increasing the cell potential for enhanced oxygen reduction.
Basic Fuel Cell Operation

1. Reactant transport
   • Efficient delivery of reactants - local flow field and mass transfer around the electrode structures (plates or cylinders in combination with porous electrodes)
   It is important to ensure active access to the electrode surface

2. Electrochemical reaction
   • Choosing right catalyst and carefully designing reaction zones

3. Ionic (and Electronic) Conduction
   • Thin electrolyte for ionic conduction, without fuel cross over

4. Product Removal
   • “Flooding” by product water can be major issue of the cell
Global aim illustrated by an example
Focus on the sulfide-driven power plant “Regenesis Technol.”

A solution of sodium sulphide (Na$_2$S$_2$) in water is fed to the negative electrode

A sodium tribromide (NaBr$_3$) solution is fed to the positive electrode

2Na$_2$S$_2$ → Na$_2$S$_4$ + 2Na$^+$ + 2e$^-$

NaBr$_3$ + 2Na$^+$ + 2e$^-$ → 3NaBr

Picture of the 100-MWh electrical energy storage facility being installed in Cambridgeshire, England.
Specific aims illustrated by example
Focus on the electrode design

The calculated cell voltages have a precision in the range of few tens of mVs and so are sufficient to predict the correct ranking of the different shapes.

The method has proved to be valid and helpful for saving time and resources

By the way

THE UNIVERSITY OF CRAIOVA  CHEMISTRY FACULTY

Dpl. Eng. Marius Constantin Mirica

Doctoral Thesis
ELECTROCHEMICAL REACTORS WITH ASYMMETRICAL CURRENT DENSITIES

Coordinator: Prof. dr. Mircea PREDA

2004
Cathode oxygen reduction reaction (ORR): $2O_2 + 8H^+ + 8e^- = 4H_2O$.

Focus on the cathode hydrodynamics
A version of a design solution

- Electrode cell for simultaneous intensive aeration accompanied by oxygen reduction

- A chamber with cylindrical electrode and ejector gas distributor; liquid phase at forced circulation by using a pump

- Reference to previous studies showed compatible energy consumption, thus, reasonable application of such a device.
The cathode chamber

Table 1  Geometry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimension (m)</th>
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<tbody>
<tr>
<td>$D_c$</td>
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<tr>
<td>$D_e$</td>
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<tr>
<td>$d_1$</td>
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<tr>
<td>$d_2$</td>
<td>0.010</td>
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<tr>
<td>$d_3$</td>
<td>0.004</td>
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<tr>
<td>$d_4$</td>
<td>0.015</td>
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<tr>
<td>$d_5$</td>
<td>0.080</td>
</tr>
<tr>
<td>$G$</td>
<td>0.032</td>
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<tr>
<td>$H_c$</td>
<td>0.45</td>
</tr>
<tr>
<td>$H_e$</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Ejector and column schematics:
1 is column, 2 cylinder electrode, 3 air ejector, 4 ejector diffuser, 5 ejector nozzle.
TWO DESIGN VERSIONS FOR THE EJECTOR

Case 1 (left): Ejector is above, gas-liquid flow goes down into the cylindrical space, gas is discharged into the upper cap.
Case 2 (right): Ejector is below, gas-liquid flow goes up into the cylindrical space, separation above and liquid circulation below along the periphery.

In the ejector: the primary fluid is water, gas is aspirated, which is the secondary fluid.

Gas is aspirated into the inlet pipe of the suction chamber of the ejector, driven by the pressure created by the liquid flow.

Attention: Pay attention to the specific geometric parameters of the ejector and their values. The diagram is given separately!
A model has to be defined that takes into account:

1) Full hydrodynamic description (CFD) using the mixture model that accounts of
   - Buoyancy effect from the gas content
   - Viscosity effects due to gas content
   - Relative velocity between the gas phase and the liquid phase

2) A primary current distribution model (Ohm’s law for ionic conduction in the electrolyte domain)

3) Full electrode kinetic expressions (Butler-Volmer expressions)
   [including the influence of both activation and concentration over-potential, where concentration over-potential depends only on an input parameter, the boundary layer thickness, and not on a real salt concentration distribution]

4) Diffusion-convection equation (full current distribution).
NUMERICAL MODEL AND PROCEDURE

- the continuity equation

\[
\frac{\partial}{\partial t} (\rho_m) + \nabla \cdot (\rho_m U_m) = 0
\]

- the momentum equation

\[
\frac{\partial}{\partial t} (\rho_m U_m) + \nabla \cdot (\rho_m U_m U_m) = -\nabla P + \rho_m g + \nabla \cdot [\mu_m (\nabla U_m + \nabla U_m^T)] + F + \nabla \cdot (\alpha_L \rho_L u_{rl} u_{rl} + \alpha_G \alpha_G u_{rg} u_{rg})
\]
Simulation domain
Refreshment over previous results
Overview of previous results (refreshment)

Various computational aspects have been resolved

• The conservation equations for mass and momentum have been solved to resolve the convective flows.
• Mesh requirement and parallel computing has been resolved.
• Solution algorithms have been fixed up.
• Velocity vectors and density contours in the cathode channel at different locations have been determined
Overview of previous results (refreshment)
Example solution contours over various flat planes
13th International Multidisciplinary Scientific GeoConference

FLOW MODELING OF A SULFIDE-DRIVEN FUEL CELL: THE CATHODE CELL WITH EJECTOR MIXER

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ABSTRACT
Oxidation of sulfide from Black Sea water for energy generation by sulfide-driven fuel cell is considered. A serious problem is the slow cathode oxygen reduction reaction (ORR): 2O₂ + 4H⁺ + 4e⁻ → 2H₂O. A solution is found by designing a cell with forced circulation by means of ejector. A cathode chamber with cylindrical coaxial electrode is proposed. Regarding the transport properties of the cathode area, the flow regime in the cathode compartment is studied. The task is solved by numerical modeling and simulation. The model can be combined with the current distribution model (Ohm’s law for ionic conduction), the electrode kinetic expressions (Butler-Volmer) and a diffusion convection equation for the ionic transport and can be implemented for complete description of current distribution and cell voltage thus promoting future analyses of the energy-storage system.

Introduction
- Black Sea water contains enormous amount of hydrogen sulfide estimated as 4.6 bill. t and this amount is increasing progressively.
- The sulfide is a potential source of energy, provided it could be converted by specialized chemical processing.
- It is most convenient to convert chemical energy directly to electrical energy involving electrochemical devices.
- The aim of this study is to formulate a flow model of the cathode cell and to characterize the flow field in view of increasing the cell potential for enhanced oxygen reduction.

Details of cathode cell design and the model
- The task is solved by numerical modeling and simulation.
- Commercial computational flow dynamics (CFD) software was used.
- A two-phase quasi-homogeneous mixture model is formulated and used in coupling with k-ε turbulence model.
- For details, see [1, 2].

Results
- Pressure p (kPa), velocity U (m/s) and gas holding c distribution in gas-liquid flow field of ejector and column
- Ejector and column velocity distribution (m/s)
- Energy dissipation rates c_U in the vessel increasing strongly and affect oxygen mass transfer by shifting the mass transfer coefficient k to larger values according to the equation. The trend is largely observed in the inner cathode area.
- Maintenance of c_U in the ]0.1 to 100 [m²/s]

References

Acknowledgement
The study is part of Project HYDULFCELS supported by Bilateral Project Programme 7.

Conclusions
- A flow model of the cathode compartment of a sulfide-driven fuel cell is formulated and its flow regime is explored.
- The key parameters of the flow field, i.e. static pressure, fluid velocity, phase volume fraction, and kinetic energy dissipation rate are determined.
- Prognostic values of the mass transfer coefficient show wide 3-fold variation across the cathode surface, namely, (0.6±10⁻⁶ to 15±6×10⁻⁶ m²/s) and imply strong influence of the flow regime over the anode diffusion.

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Characteristics of the ejector chamber

Pressure distribution (static pressure, kPa)
Characteristics of ejector chamber

Phase volume fraction
Characteristics of ejector chamber

- Velocity (m/s) distribution in air-flow plane
Characteristics of ejector chamber

- Performance close to electrode surface
Characteristics of ejector chamber

Velocity radial profiles over the electrode surface, e.g. $r=0.04\text{m}$, and near to it ($r=0.035\text{m}$, $r=0.045\text{m}$); $r$ is radial coordinate."
Characteristics of ejector chamber

Example velocity distribution (in m/s) over the solid-liquid interface (the cathode); radial coordinate $r$ varies within the range +/- 5mm.)
The framework of further studies:

(1) mesh refinement and
(2) further cell geometry
Mesh Refinement
or
What has been done on the project between the two recent meetings?

(1) Mesh 3 was elaborated for a study with increased number of cells from 700000 to 1.1 mln.

(2) Mesh 4 was elaborated for another study with further increase of the NC from 700 000 to 3.5 mln.

(3) Solutions for these discretizations of the numerical scheme

(4) New RESULTS obtained
Mesh refinement

0.14 mln cells

1.1 mln cells
Focus on the cathode active surface
Comparison of mesh refinements 3 and 4

Example with about 1mln cells.

Resolution 2mm allowing enhanced interpolation down to 200 µm.
0.1 mln cells

1 mln cells
Comparison of velocities at different cell density

Case of 0.1 mln cells

Case of 1 mln cells
Comparison of velocity contours
0-500 μm off the electrode internal surface
Comparison of velocity contours
0-500 μm off the electrode external surface

500 microns

1 mln cells

200 microns

500 microns

0.1 mln cells

200 microns
Mass transfer is important
Characteristics of ejector chamber

- Flow radial $\epsilon_T$ – as determined by the equation

$$k_L = \frac{2}{\sqrt{\pi}} \sqrt{D_{ab}} \left( \frac{\epsilon_T \rho_L}{\mu_L} \right)^{1/4}$$
Characteristics of ejector chamber

Flow radial $\varepsilon_T$ – profile corr. to levels L, M, U
Process evaluation and estimates

- Liquid-phase mass transfer coefficient. (prognostic values)

<table>
<thead>
<tr>
<th>Position</th>
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<th>0.04</th>
<th>10</th>
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<td></td>
<td>15.6x10⁻⁴</td>
<td>6.24x10⁻⁴</td>
<td>0.66x10⁻⁴</td>
<td>2.7x10⁻³</td>
<td>5x10⁻³</td>
<td></td>
</tr>
</tbody>
</table>
The framework of further studies:

(2) Study another cell geometry
2. The framework of the further study:

solution of further cell geometry and what is intended to be done

to uncover the basic relationships of the operating variables and cell design
In conclusion

The framework of further studies further cell geometry

Characterization of a fuel cell (FC) cathode chamber (equipped) with ejector mixer in view of (focused on) intensification of the oxygen reduction reaction (ORR).
Further work

- Further work is needed to uncover the basic relationships of the operating variables and cell design, namely, liquid flow rate and nozzle geometry, as well as the geometry of the cell cross section, e.g. cylindrical or rectangular.
- Essentially, the model in its present form can be combined with the current distribution model (Ohm's law for ionic conduction), the electrode kinetic expressions (Butler-Volmer) and a diffusion convection equation for the ionic transport and be implemented for complete description of current distribution and cell voltage thus promoting future analyses of the energy-storage system.
Acknowledgement

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Thank you!

Important references