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An Electrochemical Oxygen Pump Model – A Tool for Sensor Optimization

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Abstract

Electrochemical oxygen pump sensors are increasingly important in a range of industrial sensing applications. However, their development has traditionally been based on inefficient empirical approaches. We have built a detailed finite-element model of an oxygen pump electrochemical sensor that is able to simulate the distribution of oxygen within sensor components under a range of conditions. This has been used to predict key performance parameters such as the steady state output current as a function of oxygen concentration, the startup characteristics and the transient response to a step change in oxygen concentration. The model is a powerful tool enabling multiple design concepts to be compared without the need for time consuming prototype sensor construction.

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Keywords: oxygen sensor; model; simulation; finite element

1. Introduction

Electrochemical oxygen gas sensors for industrial safety applications have traditionally been based on consumable lead anode systems [1]. However, legislation to eliminate this harmful substance and demands for longer life and improved performance are driving migration to pump approaches based on fuel cell technology. The operating principle of an oxygen pump sensor is illustrated in Fig. 1. Oxygen enters the sensor via capillary

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diffusion from the top of the sensor where it combines with protons provided by the electrolyte and electrons supplied from the external circuit to produce water. Electrolysis of water at the counter electrode produces oxygen gas and protons, and supplies electrons to the external circuit. Protons are transported through the electrolyte from the counter electrode (anode) where they are produced to the sensing electrode (cathode) where they are consumed. The current flowing through the external circuit is proportional to the oxygen concentration. Because the reduction of O_2 is not spontaneous at the Pt/air rest potential, the sensor requires electrical power. In order to keep a well-defined kinetic constant for oxygen reduction at the sensing electrode, the sensor is operated in a potentiostatic circuit with the reduction bias applied to the sensing electrode with respect to a reference electrode.

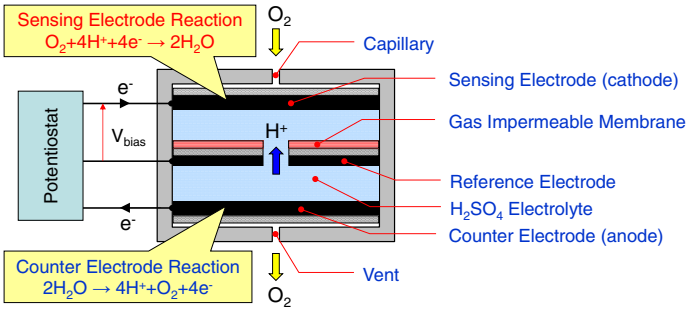

Fig. 1. The oxygen pump sensor operating principle.

To accelerate and reduce the cost of developing and optimizing the design of oxygen pump sensors, it is necessary to limit the current reliance on building and testing prototypes for every variant. We have constructed a detailed finite-element model of an axially-symmetric oxygen pump electrochemical sensor (Fig. 2) to address this need using COMSOL™ Multiphysics simulation software version 4.3b [2]. The mechanisms required to provide an adequate description of the system include (a) gas phase mass transport in free space and porous media, (b) oxygen and nitrogen transport in the electrolyte, (c) ionic current transport in the electrolyte and within porous electrodes, (d) electrode kinetics coupling the electric current transport and oxygen transport, (e) porous electrode double layer capacitive effects and (f) gas phase transport in the diffusion limiting capillary barrier.

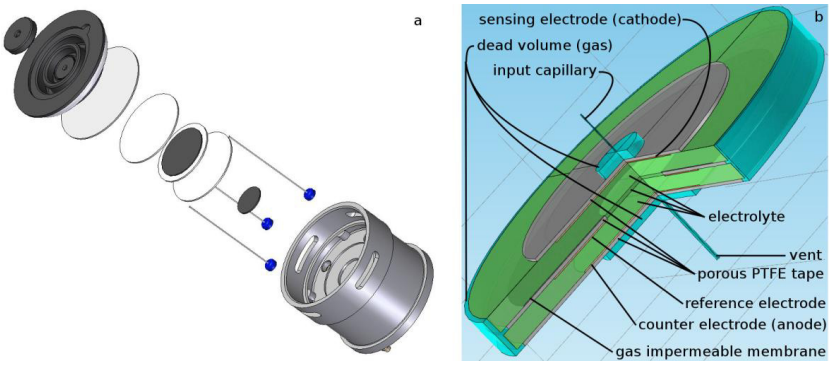

Fig. 2. (a) Typical electrochemical oxygen pump design; (b) axially symmetric sensor model geometry.

2. Model Details

In the input capillary, vent and dead volumes we model chemical species transport in gas phase. We include diffusion as well as flow, due to the fact that at the sensing electrode the oxygen is consumed, and creates a pressure

drop across the input capillary, which in turn causes gas to flow through the capillary. The same happens at the counter electrode but in reverse, the pressure being higher on the sensor side of the exhaust vent, where oxygen is produced. In the porous PTFE (polytetrafluoroethylene) tape and porous electrodes we model gas phase chemical species transport in porous media. The species that we consider in the current model are oxygen, nitrogen and water vapor.

For modeling species transport in free space as well as in porous media we use the COMSOL™ feature "Reacting Flow in Porous Media". It employs Maxwell-Stefan diffusion and Stokes flow in free space [3,4], and Maxwell-Stefan diffusion (with Bruggeman models for effective mass transport parameters) and Stokes-Brinkman flow in porous media [5]. This also provides the necessary coupling to the electrochemistry and species transport in liquids.

In the electrolyte (5M H_2SO_4 in porous glass fiber paper) and electrodes (porous platinum catalyst) we model the electric current flow and electric potential distribution. The electrolyte is also considered as a third phase in the porous electrodes, with a fixed volume fraction. The current flow through the electrolyte is modeled by considering the electrolyte as a conducting medium with an effective conductivity using the COMSOL™ feature "Secondary Current Distribution" [6].

In the electrolyte we also model oxygen and nitrogen transport in the liquid phase in porous media using Fick diffusion with a Millington and Quirk model for the effective diffusion coefficients provided by the COMSOL™ feature "Species Transport in Porous Media".

An essential requirement in modeling the oxygen pump sensor is the coupling of electric current distribution and species transport (both gas and liquid) through electrode kinetics that we model using "Concentration-dependent electrode kinetics" provided by the COMSOL™ feature "Secondary Current Distribution". In order to account for the large current transients at startup we also include porous electrode double layer capacity [7].

At the gas-liquid interface we implement Henry's Law for oxygen and nitrogen via fast dissolution/desorption kinetics, which is numerically more stable than imposing a boundary concentration constraint. For the gas-liquid boundary this is accomplished in the COMSOL™ model using the "Reacting boundary" in "Reacting Flow in Porous Media" and a corresponding "Flux" term in "Species Transport in Porous Media". For the porous electrode we use "Reaction/Mass transfer to other phases" term in "Reacting Flow in Porous Media" with a corresponding "Species Source" in "Species Transport in Porous Media".

For potentiostatic biasing of the reference electrode, we also need a global equation relating the total current in the reference electrode to the potential of the counter electrode, which we implement using the "Global ODEs and DAEs/Global Equation" feature. The potential of the counter electrode is adjusted such that the total electric current in the reference electrode is zero.

The gas impermeable membrane is treated as empty space surrounded by impermeable wall.

3. Results and Discussion

The model produces a detailed steady-state distribution of oxygen in the sensor (Fig. 3a), along with the oxygen flux (magenta arrows) and streamlines (yellow lines). Such distributions help to show how different component dimensions and materials affect the behavior of the sensor.

These outputs have been used to study the impact of design variations upon safety-critical sensor performance parameters. For example, the sensor signal as a function of ambient oxygen concentration (Fig. 3b) shows good agreement with practical data below 50%O_2 v/v. The startup transient of the sensor (Fig. 4a) demonstrates the impact of double layer charging, in particular the uneven distribution of the potential between the cathodic and the anodic overpotentials. From our simulations, the impact of bias potential between the reference and sensing electrodes on the transient response to a step change in the oxygen concentration between 20.9% and 0% appears minimal (Fig. 4b), while experimentally a slowdown of the sensor is observed. An extra diffusion step through the liquid film on the catalyst surface may explain the discrepancy. This is not included in our current model, but we plan to add it in the future.

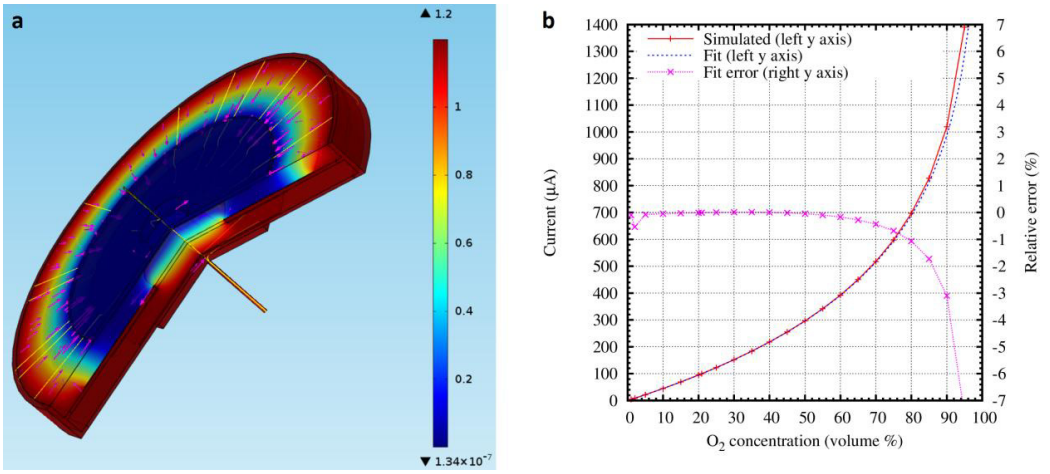

Fig. 3. (a) Oxygen distribution and flow in gas phase and electrolyte in the sensor; (b) Sensor output signal variation with oxygen concentration.

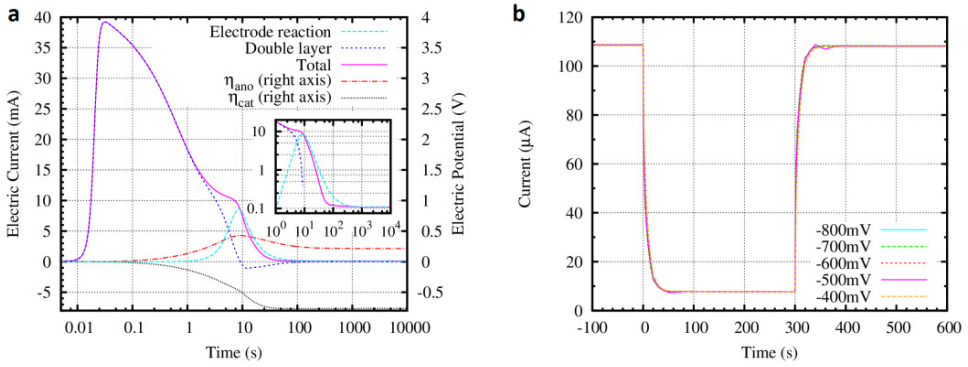

Fig. 4. (a) Startup transient: electric current (left axis), showing total current, and the contributions from electrode reaction and double layer capacity charging. The inset shows the current on a logarithmic scale. The evolution of anode and cathode overpotentials, η_{ano} and η_{cat}, respectively, is also shown (right axis). (b) Output current as a function of time for a step change in O_2, for different bias voltages.

In conclusion, we have constructed a detailed finite-element model of an axially-symmetric oxygen pump electrochemical sensor to aid the design of oxygen pump sensors, accelerating and reducing the cost of their development and optimization.

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