MOLTEN-SALT ELECTROCHEMICAL MODELING AND ITS BENCHMARKING WITH COPPER ELECTROPLATING SYSTEM

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Three dimensional (3D) electrochemical modeling in a framework of Computational Fluid Dynamics (CFD) was prepared and based on the mass transfer controlled electro-transport behavior that appears in a molten-salt electrolytic system. The modeling approach in this study is focused on the mass transport and current arising from the concentration and overpotential in a specific cell configuration. This comprehensive approach was applied to the copper electroplating model in a rotating cylinder hull (RCH) cell system for validated model benchmarking.

I. INTRODUCTION

A nuclear fuel cycle based on pyroprocessing technology offers substantial improvements in waste management, proliferation resistance and economic potential compared to the wet processing used in leading countries of nuclear power technology (Ref. 1). Pyroprocessing is a technology involving electrochemical treatment using a molten salt medium. The pyrochemical process operated using a high-temperature molten salt electrolyte is cost intensive since experiments are implemented under a radioactive environment.

The most effective way to accelerate the development of these technologies is to formulate physical models of the underlying electrochemical and transport processes. In addition, an integrated multi physics simulation offers an efficient approach to the design, testing, and implementation of these processes.

In this study, an implementation of the electrochemical hydrodynamics modeling within a computational fluid dynamics (CFD) framework was carried out to simulate the electrorefining process. In an electrorefiner geometry, the comprehensive approach and algorithm for representing the more realistic electrochemical hydrodynamics features are described. In addition, a benchmark simulation for the proposed modeling technique with a copper electroplating system in a prepared rotating cylinder Hull (RCH) cell system is conducted to know the validity of this approach and model capability.

II. MATHEMATICAL MODEL

A CFD simulation has proven to be a useful tool in the analysis and design of electrochemical reactors. An electrotransport process occurs whenever an electric current flows between the electrodes of in an electrochemical reactor. A 3D configured cell can be modeled as an electric field problem inside the electrolyte domain with nonlinear boundary conditions at the electrodes. The electrolyte domain is governed by Navier-Stokes and continuity equations for fluid turbulence in an agitated electrochemical cell (Ref. 2).

At the appropriate electrode boundary in the 3D cell domain, Faraday's law establishes the relationship between the current (*i*) passing through the metal-electrolyte interface and conversion rate of the reactant of interest. For the reduction of reactant species *O* involving *ne* electrons for a cathodic process:

$$O + ne^- \rightarrow R \qquad (1)$$

For sufficient polarization, i.e. for $|\eta| > 50{\sim}100mV$, one of the two exponential vanished in the Butler-Volmer kinetics relation can be approximated using the empirical Tafel laws (Ref. 3):

$$i = -i_0 exp\left(-\frac{\alpha n_e F}{RT}\eta_a\right) \qquad (2)$$

On the cathode side, a negative flux is applied as the boundary conditions in a galvanostatic electrolysis:

$$i_{app} = -\int_s \; ids\,/S \qquad (3)$$

III. EXPERIMENTAL

The design of a rotating cylinder hull (RCH) cell enables a wide range of electrochemical features to be achieved in a single experiment, and is useful to benchmark the proposed model (Ref. 4). To measure the overpotential distribution along the rotating cathode surface, the experimental system was modified using an RCH cell that consists of a commercially available RotaHull set (Fig. 1). The tips of the eight Luggin capillaries made of Teflon were placed close to the rotating cathode surface. The Ag/AgCl reference electrodes with a saturated KCl solution were externally connected with a Luggin capillary probe that can be kept very close (~1 mm) to the working electrode to minimize the Ohmic resistance. The overpotentials were monitored by connecting to a multichannel recorder (e-corder ED1621, eDAQ).

IV. RESULTS AND DISCUSSION

3D electrochemical modeling in a CFD framework was based on the mass transfer controlled electro-transport behavior that appears in a molten-salt electrolytic system. To develop a comprehensive model, the focus is on the deposition of metal at the electrode. The proposed modeling approach is a technique that accounts for all possible configurations and operational alternatives of the metal refining system.

This comprehensive approach was applied to the copper electroplating model in a rotating cylinder Hull (RCH) cell system for the validated model benchmarking. This sophisticated system provides the proven model of an electroplating system that controls the electrolyte fluid dynamics and mass transport conditions. The simulated current density distribution and local overpotential measurements along the cathode are shown in Fig. 2 and Fig.3, respectively.

The proposed CFD based model can offer an efficient approach to the design, testing and implementation of the electrochemical process assessment. This deposition model provides engineers the ability to simulate the influence of the cell geometry and operating conditions in the electrochemical metallurgy industry.

Fig.1. Rotating cylinder Hull (RCH) cell system.

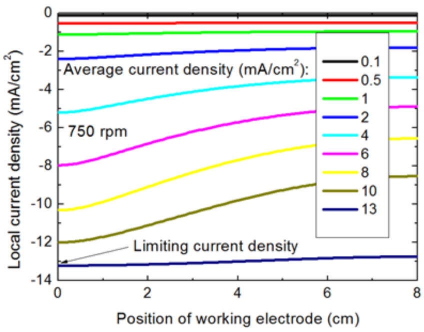

Fig.2. Simulation for local current density distribution along the cathode.

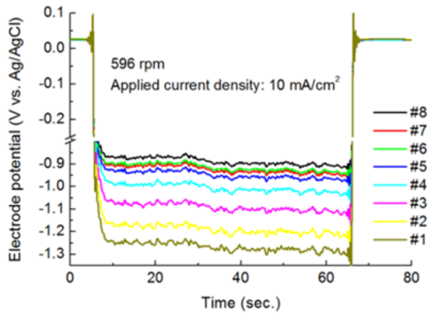

Fig.3. Measurements of local overpotential distribution.

V. CONCLUSIONS

A computational electrochemical fluid dynamics model for a metal electrorefining system was proposed on a CFD framework. Through a benchmark against the proven model of the RCH system, this modeling feature can allow the implementation of a potential-to-current polarization algorithm that allows for a more realistic spatial variation of the electrochemical kinetics.

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REFERENCES

1. IAEA, Spent Fuel Reprocessing Options, IAEA-TECDOC-1587, IAEA, Vienna, 139 (2008).
2. K. R. KIM, S. Y. CHOI, S. H. KIM, J. B. SHIM, S. PAEK AND I. T. KIM, *Journal of Radioanalytical Nuclear Chemistry*, **299**, 165 (2014).
3. A. J. BARD and L. R. FAULKNER, *Electrochemical Methods, Fundamentals and Applications*, pp. 87–136, 2nd Ed., John Wiley & Son Inc., New York (2001).
4. C. J. T. LOW, E. P. L. ROBERTS and F. C. WALSH, *Electrochimica Acta*, **52**, 3831 (2007).