

## The Influence of Natural Convective Flow on the Electrochemical Analysis

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### 1. Introduction

The molten salt reactor (MSR) is the promising next generation reactor types (Gen-IV) characterized by extreme safety by excluding severe accident that can occur due to the loss of coolant in existing light water reactors using solid nuclear fuel [1]. The one of advantages of the reactor is the molten salt used as fuel and coolant that can be manufactured based on the previously developed pyro-processing to manage spent fuel.

Since the reactor retains the high temperature molten salts, the corrosion will be a challenging issue to maintain structural integrity. As the issue persists while the reactor operates, it is necessary to develop the salt monitoring system that can measure salt composition in real time. In this regard, the electrochemical analysis is generally widely used in molten salt experiments and has an advantage in that immediate evaluation is possible. However, as the electrochemical analysis is sensitive, it can be easily affected by undesired flows when analyzing the measured data. Therefore, recent studies on natural (free) convection, which have not been well considered, are being conducted under the assumption that convective flows induced near electrode can cause inaccurate measurements [2].

The phenomenological study was conducted with use of COMSOL Multiphysics 6.0 [3] to identify effect of natural convection for the one-electron transfer model redox systems ( $\text{Sm}^{3+}/\text{Sm}^{2+}$ ,  $\text{Cr}^{3+}/\text{Cr}^{2+}$ ). The simulation results of electrolysis (CV, CA) were compared by changing the term contributing to the mass transport equation.

### 2. Background theory

#### 2.1 The influence of convection on the electrode

When flux density of dissolved ion traveling to the electrode is governed by diffusion, migration and convection which is expressed in Eq. (1). The subscript  $r$  represents a reactant.  $z$  is valence of ionic species.  $F$  is Faraday constant.  $\Phi$  is electric potential.  $D$  is diffusivity of the reactant.  $c$  is concentration.  $v$  is flow velocity of fluid.

$$J_r = -z_r u_r F c_r \nabla \Phi - D_r \nabla c_r + c_r v. \quad (1)$$

Since the reaction of minor ionic species in a solution containing excess supporting electrolyte, it should be permissible to neglect the contribution of ionic migration to the flux of the reacting ions and the Eq. (1) becomes,

$$J_r = -D_r \nabla c_r + c_r v. \quad (2)$$

In an electrolysis, the bulk convection alone does not cause a net current due to the electroneutrality. As shown in Eq. (3-4), however, although the convection cannot contribute to current, convection still can affect concentration gradient with supplying reactant to the electrode surface [2]. It means that the convection regulates the current.

$$i_r = z_r F J_r = z_r F D_r \nabla c_r. \quad (3)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \vec{v} \nabla c. \quad (4)$$

#### 2.2 Natural convection effect on the electrolysis

The natural convection due to density gradient in the vicinity of electrode may occur as the consumption of reactants and formation of products. Especially, when we use the macroelectrode, the accordance of density difference cannot be avoided phenomena as the buoyant force due to the gravitational acceleration contributing the flow of solution.

The changes in the density of the electrolyte can be accompanied by two reasons. One is the electrochemical conversion near the electrode due to redox reaction such as the consumption of reactant and formation. The other is temperature gradient resulting from the change in enthalpy due to exothermic or endothermic reaction [5].

#### 2.3 Modeling of density driven convection

The mass transfer of reactant is governed by mass conservation equation (5). In addition, in order to solve mass transport equation, continuity equation for an incompressible Newtonian fluid and Navier-Stokes equation are introduced in Eq. (6) and (7) respectively,

$$\partial_t c_O = -\nabla \cdot J_O. \quad (5)$$

$$\frac{\partial c_O}{\partial t} = \nabla \cdot (c_O v) - \nabla \cdot (D_O \nabla c_O) = 0. \quad (6)$$

$$\rho_0 \frac{\partial c_O}{\partial t} + \rho_0 (v \cdot \nabla) v = \nabla p + \mu \nabla^2 v + \Delta \rho g. \quad (7)$$

The density driven convection focuses on buoyant force in gravity field.  $\Delta \rho$  is the density change caused by concentration gradient, expressed as Eq (8). Since the total amount of O and R at the electrode-electrolyte interface, Eq. (8) can be simplified as Eq. (9). Thus, based on the assumption that the both diffusion coefficient of oxidant and reductant are the same, we can derive the density difference as expressed in Eq. (10).

$$\Delta \rho = \beta_O (c_O - c_b) + \beta_R (c_R - c_b). \quad (8)$$

$$\Delta \rho = \left( \beta_O - \frac{D_O}{D_R} \beta_R \right) (c_O - c_b) = \beta_c (c_O - c_b). \quad (9)$$

$$\Delta \rho = (\beta_O - \beta_R) (c_O - c_b) = \beta_c (c_O - c_b). \quad (10)$$

Equations (11-12) show the heat flux at the surface of electrode due to the change of enthalpy. In this case the normal heat flux is proportional to the normal mass flux. In addition, based on the Fourier's law, the heat flux can be expressed with the temperature gradient [6]. Thus, we have the simplified temperature gradient based on the calculated diffusion length and thermal length ( $L_{diff} = \sqrt{D_O t}$ ,  $L_{therm} = \sqrt{\chi t}$ ).

$$q_{z=0} = -\Delta H \times D_O \frac{\partial c_O}{\partial z}, \quad q_{z=0} = -k \frac{\partial T}{\partial z} \quad (11)$$

$$\Delta T \sim -\Delta H \Delta c_O \frac{D_O L_{therm}}{k L_{diff}} \Rightarrow -\Delta H \Delta c_O \frac{D_O}{k} \sqrt{\frac{\chi}{D_O}}. \quad (12)$$

Figure 1 shows the schematic diagram for numerical analysis. For the CA simulation, electrical current density is related to the mass flux. Fig. 2 shows the mesh geometry for the numerical analysis. The mapped mesh is used in the vicinity of an electrode and free triangular mesh is used for remained domain. The computing time is about tens of seconds for all cases.

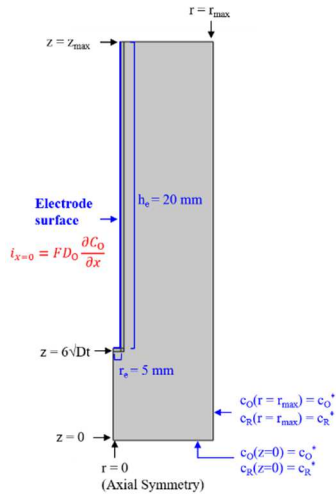


Fig. 1. Schematic diagram of the electrochemical cell.

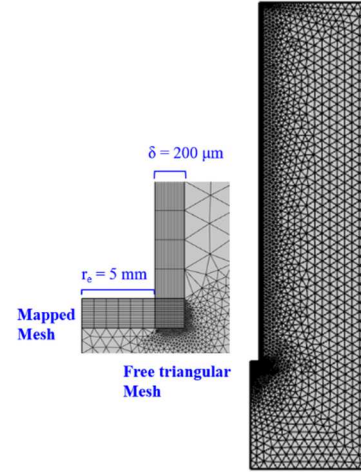


Fig. 2. Used mesh geometry for the calculation.

### 3. Results and discussion

Figure 3 shows the chronoamperometric curve in order to verify the natural convection effect. The black dotted plot is corresponded to the effect of diffusion only. The red dotted is corresponded to the effect of convection. The both plots show that the current decreases as the time increases. This is because the reactant in the vicinity of electrode is depleted with time elapsed. As expected, the due to the natural convection effects, diffusion-controlled current shows plateau in about after 50 seconds. On the other hand, for the diffusion only condition, the current with time tended to decrease continuously. It seems that the thicker diffusion boundary layer is formed rather than diffusion-controlled condition.

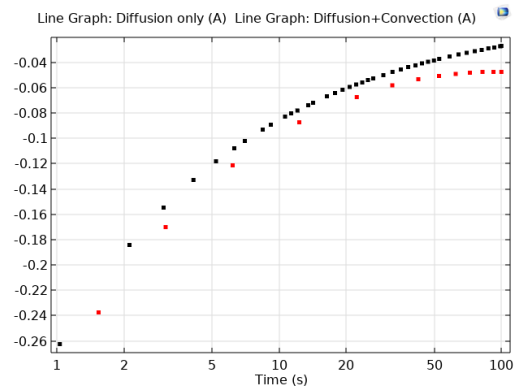


Fig. 3. The numerical results of chronoamperometric curve for the LiCl-KCl-13 mM CrCl<sub>3</sub> at 773 K.

Figure 4 shows the result of concentration and velocity profile to verify the effect of natural convection. The both results are corresponded to the last time step for the calculation (100 s). The concentration profile shows the change in density. The result shows Rayleigh-Bernard convection which is type of natural convection. Contrary

to the expectation that an upward flow will occur near the electrode due to the buoyancy as the lack of reactant near the electrode, a downward flow was found. It seems that this is because the relatively high density as more reaction occurred at the bottom of the electrode.

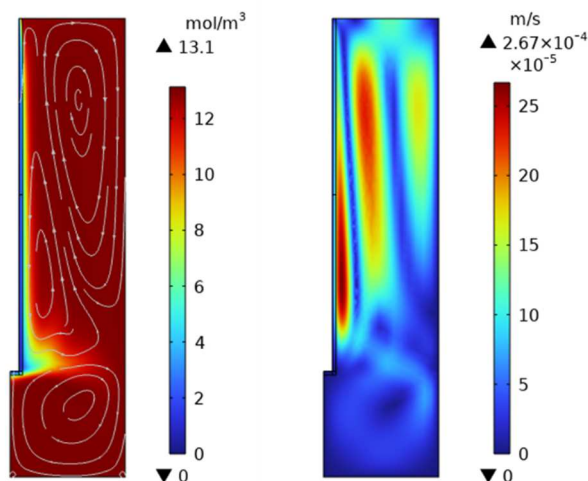


Fig. 4. Concentration profile (left), velocity profile (right) for the LiCl-KCl-13 mM CrCl<sub>3</sub> at 773 K.

#### 4. Summary and Future works

The phenomenological study was conducted in order to investigate the natural convection effect. Based on the theoretical analysis for the two difference conditions, chronoamperometry curve showed the effect of density driven convection due to the difference of concentration.

The understanding of the natural convective flow mechanism in high temperature molten salt system can brings us to the more accurate concentration measurement of soluble-soluble redox couples. The more studies will be required for the geometry effect of electrode and physical property effect of electrolyte such as concentration and density of redox species. Thus, the further studies will be made up to verify the results experimentally and numerically as soon as possible.

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