

Electrodeposition of charged particles onto fuel cell coolant channel walls

1. Introduction

The rapid development of fuel cells has been a matter of great importance in the last two decades because they are able to convert externally supplied H_2 to electricity with a very high efficiency [1,2]. However, there exist a number of problems that need to be overcome before this technology can be applied into reality. For instance, a huge amount of heat might be produced during the operation period of some kinds of fuel cells such as phosphoric acid fuel cells (PAFCs) and solid oxide fuel cells (SOFCs), which can significantly increase their operation temperatures so that the fuel cells might be ruined [3,4]. Therefore, a cooling system is needed to ensure fuel cells to run in an appropriate temperature range. Of two types of coolants (water or air) currently being used for fuel cells, water is preferred because its thermal conductivity is approximately twenty times higher than that of air. However, after long-term operation charged particles can leach into the coolant flow, increasing the conductivity to unacceptable levels. When these charged particles move with the coolant flow, they will be attracted towards the channel walls because of electrokinetic forces, thereby causing deposition of charged particles onto the walls [1]. This phenomenon is called electrodeposition that has been widely investigated in industry [5-8]. This process involves multidimensional phenomena that include transport of charged particles via diffusion, electromigration, and convection. Various computational modeling methods have been used to simulate electrodeposition processes under a variety of conditions. For instance, pioneering work by Griffiths et al. [9] was carried out to develop one and two-dimensional numerical models describing electrodeposition of metal species onto high aspect-ratio molds. Their one-dimensional model describes dissociation, diffusion, electromigration, and deposition of multiple ionic species; their two-dimensional model focuses on

single-species transport including forced flow due to bath stirring and buoyancy-induced natural convection. Especially, finite element method (FEM) is believed to be one of the most powerful computational modeling methods in understanding these complex, coupled phenomena and aiding in elucidating the mechanisms involved [10-12]. The goal of this work is to predict the electrodeposition of charged particles onto the internal fuel cell coolant channel walls. A FEM model [13-21] will be developed to determine the effects of various parameters (i.e., particle size, charge density, flow rate of the coolant etc.) on the electrodeposition of charged particles.

2. Governing equations

Electrodeposition of charged particles onto the internal fuel cell coolant channel walls is a complicated process, which is affected by a variety of factors involving electrokinetic force derived from anodes and cathodes of fuel cells, hydrodynamic force as well as buoyancy force from coolant fluid (water). In order to efficiently model the electrodeposition process, following two assumptions were made:

1. The particles are in a suspension so dilute that they do not experience significant agglomeration.
2. Given the dilute nature of the suspension, the removal of particles from the fluid over time is not expected to affect the hydrodynamic properties of the coolant.

2.1. Coolant fluid flow

Fluid flow in the coolant channel follows Navier-Stokes equations:

$$\rho \frac{\partial \vec{\mu}}{\partial t} - \eta \nabla^2 \vec{\mu} + \rho (\vec{\mu} \cdot \nabla) \vec{\mu} + \nabla p = \vec{F} \quad (1)$$

$$\vec{\mu} \cdot \nabla = 0 \quad (2)$$

Where $\vec{\mu}$ stands for the velocity field vector, ρ is the fluid density, η is the dynamic viscosity, and p is the pressure

2.2. Convection, migration and diffusion of charged particles

The material balance of charged particles comes from the equation:

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c - zbFc \nabla V + c\vec{u}) = R \quad (3)$$

Where D is diffusion coefficient of charged particles, R is reaction rate ($=0$ here), c is concentration of charged particles, F is Faraday's constant (96485.34 C/mol), z is charge number of particles, V is applied electric potential, b is mobility of charged particles, \vec{u} is fluid velocity.

2.3. Sorption of charged particles onto the walls

The Random Sequential Adsorption model has been widely used in the prediction of charged particle sorption. Based on the forces exerted on adsorbing particles including interactions between these particles and those adsorbed ones on the walls along with the hydrodynamic driving force and buoyant force, the rate of change in surface coverage is represented non-dimensionally by:

$$\frac{d\Theta}{d\tau} = B(\Theta) - \bar{K}_d \Theta \quad (4)$$

Where $\Theta = \frac{\tau a^2 N_s}{S}$ is dimensionless surface coverage, a is particle radius, N_s is the

number of particles on surface, $\tau = \frac{t\pi a^2 j_0}{0.547}$ is the dimensionless time, J_0 is the

normal component of initial particle flux to uncovered interface, \bar{K}_d is

dimensionless desorption constant. For irreversible adsorption, $\bar{K}_d = 0$

3. Formulation and solution

3.1. Formulation

The length and radius of the coolant channel are 1 and 0.3 cm, respectively. The coolant must absorb heat from the channel walls, therefore making the temperature of

the coolant constant at 348 K. The diameter of the charged particles is estimated to be in the range of 20~50 nm. They are so tiny that we do not need to take their buoyancy and gravitational forces into account. The various parameters that will be used in COMSOL simulation are shown in table 1.

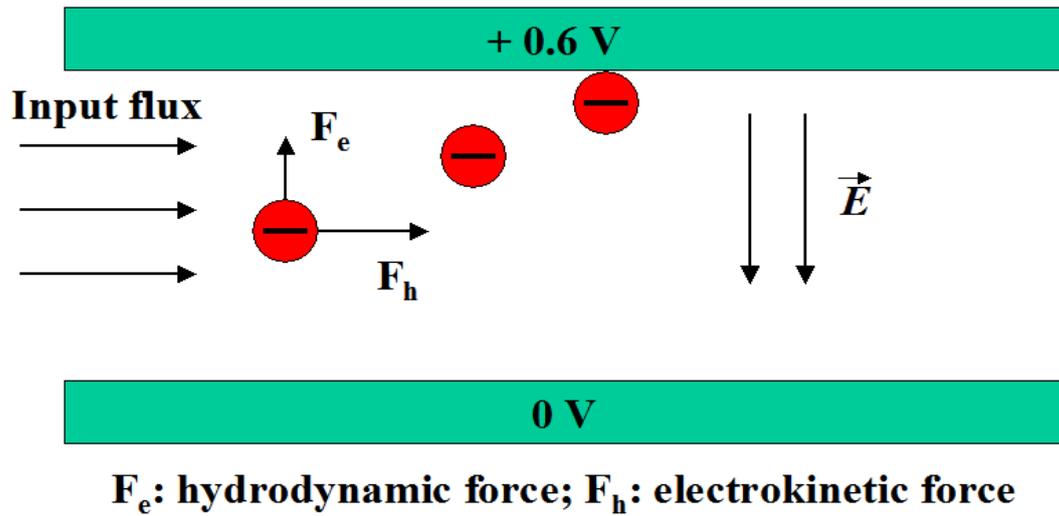


Figure 1. Scheme of charged particles in a fuel cell coolant channel.

Table 1 The physical properties of the coolant and charged particles

Coolant's density	1.05 g/ml
Coolant's dynamic viscosity	7 miliPa.second
Coolant's thermal conductivity	0.35 W/m.K
Coolant's heat capacity	3557 J/Kg K
Coolant's electrical conductivity	0.5 μ S/cm
Charged particle's diameter	20 ~ 50 nm
Charged particle's density	1.05 g/cm ³
Diffusion coefficient of charged particle in coolant	5 x 10 ⁻¹³
Charged particle's molar concentration in coolant	2.5 x 10 ⁻⁷ M
Charge number of particles	1.2 x 10 ³ /particle
Charged particle's mobility in coolant fluid	7 x 10 ⁻⁴ cm ² /V sec

3. 2. Solution

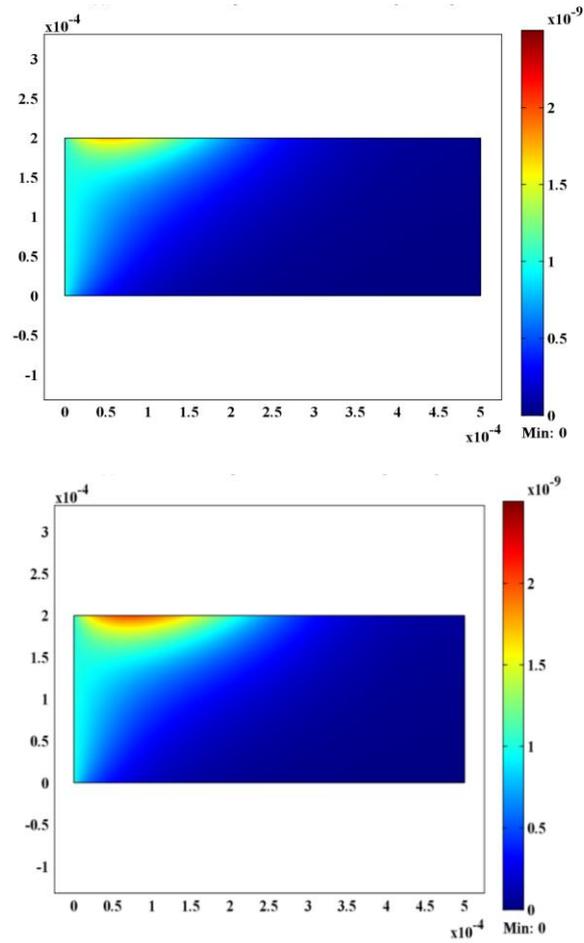


Figure 2. The charged particle concentrations in the coolant channel (left: $T=20$ S; right: $T=35$ S).

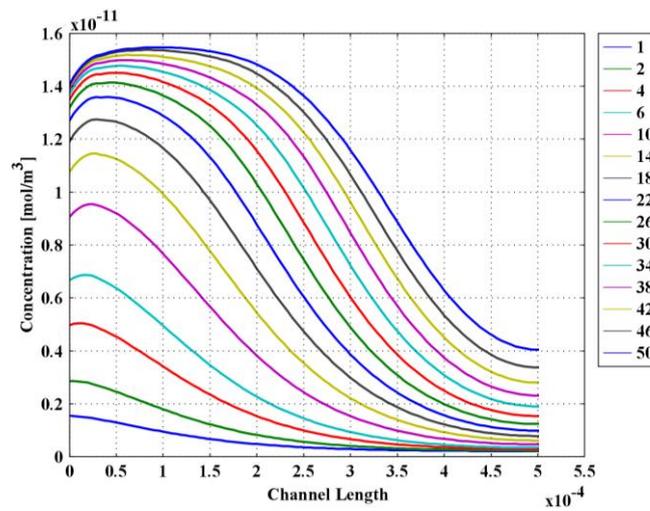


Figure 3. The concentrations of charged particles adsorbed onto the channel walls as a function of time.

The particle concentrations in the coolant channel at $T=20$ S and $T=35$ S is illustrated

in Figure 2. It would take months under real conditions to reach notable level of deposition in fuel cell coolant channels. In order to have a significant deposition rate onto the channel walls in a relatively short simulation period, the diffusion coefficient of charged particles was increased 500 times. As a result, a significant increase of deposition concentration of charged particles along the coolant channel walls could be observed in a short time. The deposited particle concentrations on the channel walls are shown in Figure 3. We can see that the largest portion of deposition occurred near the inlet region. Such an apparent increase of deposition with time through the whole channel length is because of the less desorption rate in the channel with an extreme low fluid velocity.

4. Validation

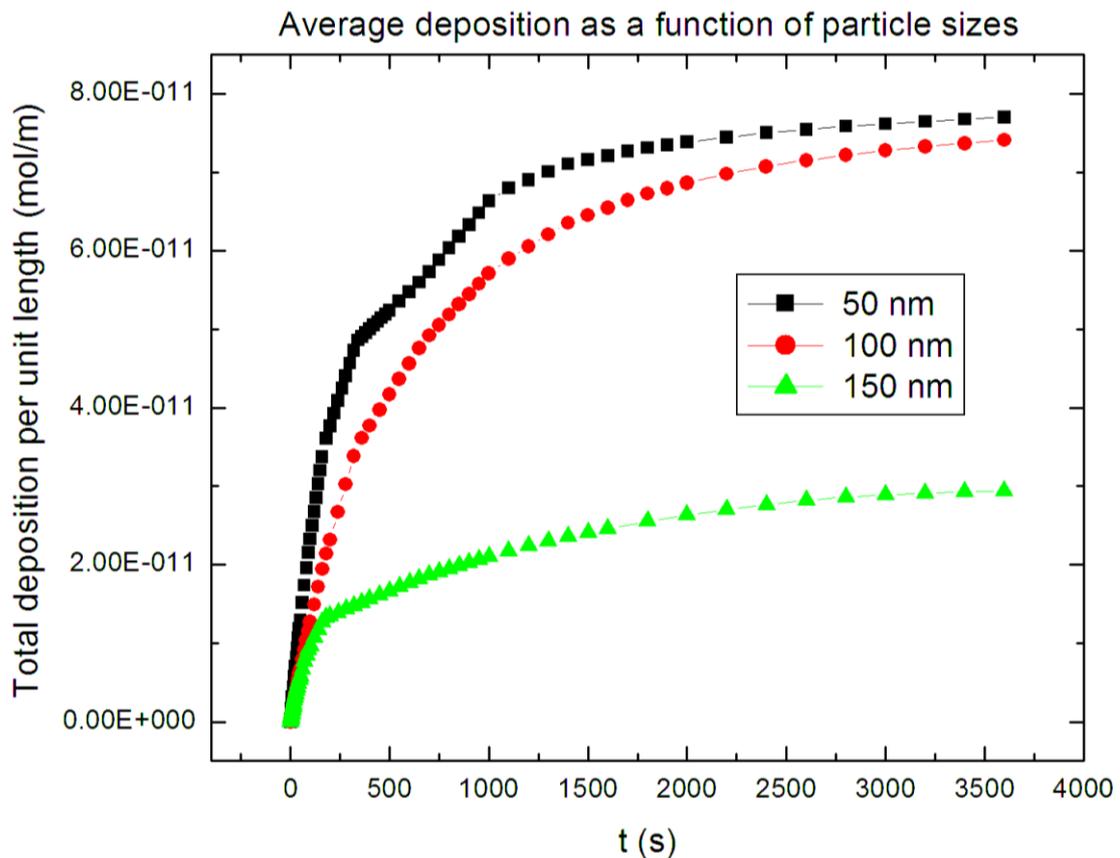


Figure 4. The plot of depositions of charged particles with different sizes as a function of deposition time.

Electrodeposition of charged particles onto the fuel cell coolant channel walls is a

complex process that is governed by diffusion and convection of charged particles as well as external electrokinetic forces between charged particles and the channel walls. It has been widely accepted that depositions of charged particles onto channel wall occur in two stages: (1) initially the walls are free of charged particles; the deposition rate is therefore predominantly determined by the interaction between charged particles and the walls; (2) as with the adsorption process proceeding, more and more charged particles attach onto the walls; as a consequence, the charged particles already adsorbed onto the walls significantly affect the sorption of the subsequent particles. Electrodeposition of charged particles onto the channel walls is believed to be very sensitive to the particle sizes, especially at the 2nd step. If the particle sizes are in nano-range (1-100 nm), the charged particles will exhibit a distinct deposition trend in contrast to bulk particles (>100 nm). This is because their much smaller sizes of nanoparticles lead them to have very unique physicochemical properties such as weaker electro-repulsive forces between nanoparticles as compared to the bulk particles. From Figure 4, we can see that at the initial stage (0~250 S) nanoparticles and bulk particles display comparable depositions. This fact reveals that the particle sizes do not exert remarkable influences at 1st step of electrodeposition. However, at 2nd step (after 250 S) it can be observed that the depositions of charged bulk particles are much lower than those of charged nanoparticles due to the strong inter-particle electro-repulsive forces, while the nanoparticles with different sizes (50 and 100 nm) show similar depositions. This fact demonstrates that the results obtained from COMSOL simulation fit well with the theory regarding the effect of particle sizes on the depositions of charged particles onto channel walls. Therefore, it can be inferred that COMSOL simulation can serve as a good modeling tool for charged particle electrodeposition onto fuel cell coolant channel walls.

5. Parametric study

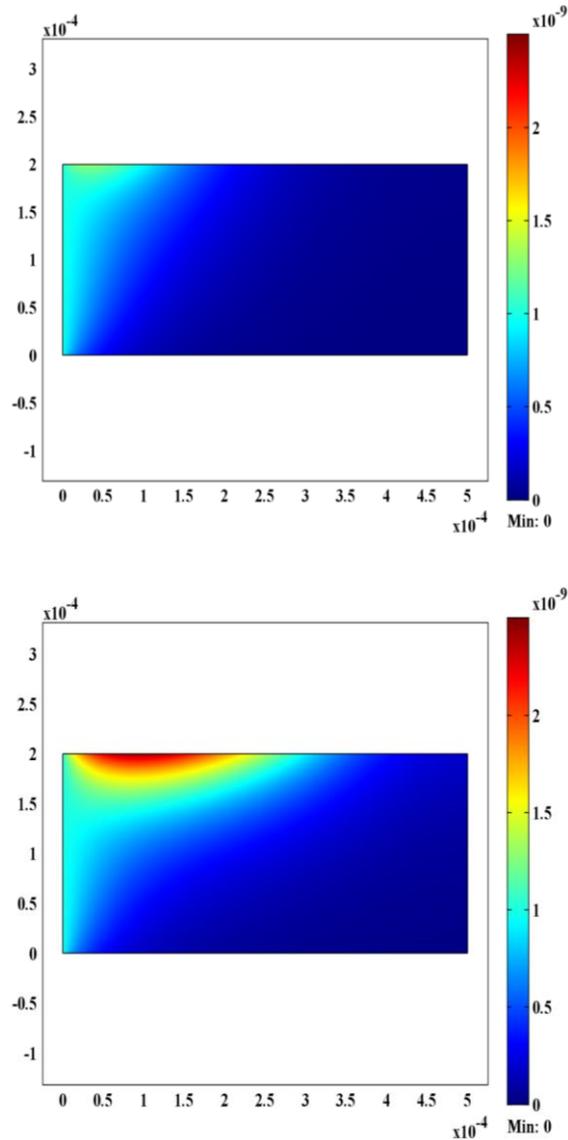


Figure 5. Charged particle depositions in the coolant channel at different particle's concentrations (left: 0.5×10^{-7} M; right: 5×10^{-7} M).

Charged particle's molar concentration in the coolant is considered to be a crucial parameter for the depositions onto the channel walls. It is therefore selected as the variable for parametric study. As shown in Figure 5, two different particle's molar concentrations were chosen at 0.5×10^{-7} and 5×10^{-7} M. Apparently, the particle's concentration could significantly influence their depositions onto the channel walls. According to the result shown in Figure 5, one can draw such a conclusion that the higher the initial particle's concentration in the coolant, the more the depositions onto

the walls occur. Therefore, in reality some filters are installed in the coolant channels to remove these charged particles. This cleanup process could dramatically reduce the concentration of charged particles in the coolant so that it generally takes several years to reach detectable particle depositions.

6. Conclusions

1. COMSOL Multiphysics has been used to simulate the electrodeposition of charged particles onto fuel cell coolant channel walls. It has been proven that this modeling method is a powerful tool to predict the electrodeposition of charged particles.

2. The predicted charged particle depositions are not uniform along the channel. More depositions occur near the inlet region.

3. The concentration of charged particles has a remarkable effect on their depositions onto the walls, i.e., the higher the particle concentration in the coolant, the more the deposition onto the walls occurs.

4. It was proven that charged particle electrodeposition onto the walls is fairly sensitive to the particle sizes. If the particle sizes are out of nanoscale (1-100 nm), the bulk charged particles will exhibit distinct electrodeposition behaviors as compared with nanosized particles.

Reference

- [1] Trimm D. L., Z. Nsan I. O., “Onboard fuel conversion for hydrogen-fuel-cell-driven vehicles” *Catalysis Reviews*, 43, (2001), 31.
- [2] Ferreira-Aparicio P., Benito M.J., Sanz J.L., “New trends in reforming technologies: from hydrogen industrial plants to multifuel microreformers” *Catalysis Reviews*, 47, (2005), 491.

- [3] Zhang J.L., Xie Z., Zhang J.J., "High temperature PEM fuel cells" *Journal of power sources*, 160, (2006), 872.
- [4] Li Q.F., He R.H., Jensen J.O., "Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100°C" *Chemistry of Materials*, 15, (2003), 4896.
- [5] Chen K. S., Evans G. H., "Two-dimensional modeling of nickel electrodeposition in LIGA microfabrication" *Microsystem Technologies* 10, (2004), 444.
- [6] Freunberger S. A., Wokaun A, Büchi F. N., "In-Plane Effects in Large-Scale PEFCs II. The Influence of Cooling Strategy on Cell Performance" *Journal of The Electrochemical Society*, 153, (2006), 909.
- [7] MARSHALL G., TAGTACHIAN S., "Growth pattern formation in copper electrodeposition: experiments and computational modelling" *Chaos, Solitons & Fractals*, 6, (1995), 325.
- [8] Poon G.K.K., Williams D.J., "Modeling of acid copper electroplating" *Journal of electronics manufacturing*, 8, (1998), 15.
- [9] Griffiths S. K., "Modeling electrodeposition for LIGA microdevice fabrication" *Microsystem Technologies*, 4, (1998), 98.
- [10] Felippa, C., (2002), "Introduction to Finite Element Method", University of Colorado.
- [11] Tezduyar T.E., "Finite elements in fluids: Stabilized formulations and moving boundaries and interfaces" *Computers & fluids*, 36, (2007), 191.
- [12] Dwivedy S.K., Eberhard P., "Dynamic analysis of flexible manipulators" *Mechanism and machine theory*, 41, (2006), 749.
- [13] FemLab User's Guide, Comsol
- [14] Welty, Wicks, Wilson, "Fundamentals of Momentum, Heat, and Mass Transfer, 3rd edition", John Wiley & Sons.
- [15] Bird, Stewart, lightfoot, "Transport Phenomena", John Wiley & Sons.
- [16] Bird et al. Transport Phenomena.
- [17] Perry's Chemical Engineering Handbook.
- [18] McCabe and Smith. Unit Operations of Chemical Engineering.

- [19] Ilic M.M., Notaros B.M., "Higher order large-domain hierarchical FEM technique for electromagnetic modeling using legendre basis functions on generalized hexahedra" *Electromagnetics*, 26, (2006), 517.
- [20] Delhom B., Richalot E., Mengue S., "FEM modeling of finite electronically controllable PBG structures" *European physical journal-applied physics*, 29, (2005), 133.
- [21] Yuan J., Kang J., Rong Y. "FEM modeling of induction hardening processes in steel" *Journal of materials engineering and performance*, 12, (2003), 589.