A novel study of the kinetics of external hierarchical nanostructures in methanol fuel cell

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Abstract. For the purpose of a direct methanol fuel cell (DMFC), this research investigates the kinetics of methanol oxidation in a porous layer consisting of external hierarchical nanostructures through 2D COMSOL simulation. Three different lengths of nanowires ($L$) were considered in simulations. The investigation showed that specific activity was reversely proportional to nanowires length and roughness factor ($R_f$). However, the current density increased by increasing $R_f$. Although the current density in case of $L = 200$ nm and 500 nm was identical with respect to $R_f$, there was a slight deviation when $L = 1000$ nm due to the changing from kinetic to diffusion controlled regime, which was identified by investigation of Thiele modulus. The catalytic efficiency for $L = 1000$ nm dropped to 50% at $R_f = 140$, whereas the high efficiency with no mass-transport limitation was achieved by shorter nanowires. Therefore, increasing $R_f$ within the simulation range resulted in increasing the total catalytic activity but simultaneously decreasing the specific activity because of the decrease in pore accessibility and catalytic efficiency of nanostructures.

1. Introduction
The high surface-to-volume ratio of nanoporous electrodes results in high catalytic surface area. [1] Therefore, there is an increasing number of nanostructures that were reported for several catalytic reactions. Hierarchical nanostructures represent one of the most significant nanostructures generating a nanoporous layer. [2] Generally, they consist of two sub-structures, macrostructures and micro-/mesostructures. [3] According to our definition, hierarchical nanostructures can be divided into two types, internal and external. The internal structures consist of macropores that work as a distributor of diffused species to the interconnected micro-/mesopores. [3] On the other hand, the external structures consist of macrostructures that grow on the electrode surface and serve as a base for the interconnected nanowires.

According to Butler Volmer equation (BV), the overall catalytic activity of the nanostructures is influenced by the reaction kinetics and the concentration of active species at the active surface. [4] The catalytic activity defines the number of reactions at the active site and the number of active sites on the nanostructures [5]. Therefore, surface $R_f$, which is defined as the ratio between the total nanoscopic catalytic surface area and the geometrical surface area [6], influences the catalytic activity through its influence on the number of active sites. In addition, the concentration of active species influences the reaction rate at the active sites due to local concentration factor in BV. [4] Accordingly, pore accessibility is an additional factor that influences the overall catalytic activity.
Specific activity (A/cm$^2$) and current density (A/cm$^2$) are experimental quantities, mostly used for determining surface catalytic activity. Specific activity, which defines the average current per the unit of electrochemical active surface area [7, 8], measures the catalytic activity based on the pore accessibility only. However, catalytic activity based one current density includes $R_f$ and pore accessibility. On the other hand, Thiele modulus and effectiveness factor are numerical values that can evaluate the catalytic activity and determine the regime of reaction kinetics. Electrode kinetics according to Thiele modulus is classified as one of two regimes, diffusion controlled (D-controlled) or reaction kinetic controlled (k-controlled). [9, 10]

Unlike many former researches that have investigated internal hierarchical structures, like reference [11], this paper investigated the kinetics in a porous layer that consists of external hierarchical nanostructures through 2D COMSOL simulation. Beside the investigation of specific activity and current density based on BV, mass-transport and pore accessibility was also examined based on Thiele modulus. Simulations were performed for the purpose of a direct methanol fuel cell.

2. Methods

2.1. Reaction kinetics
The kinetic of methanol (Red) oxidation at the anode was investigated in our simulations by considering a reaction that releases one electron and one proton, i.e., oxidizing agent (Ox). The kinetics of reactions occurring on the electrode surface is influenced by the electrode potential. [4, 12] The current-potential characteristics were determined according to BV equation, which predicts the currents resulting from the overpotential on the electrode [12]:

$$ j = j_0 \left[ C_{Ox} \exp \left( \frac{-aF\eta}{RT} \right) - C_{Red} \exp \left( \frac{1-aF\eta}{RT} \right) \right] \tag{1} $$

where

$$ j_0 = Fk^0C_{Ox}^{1-a}C_{Red}^a = Fk^0C \tag{2} $$

where $j$ is the current density (A/m$^2$), $F$ is the Faraday constant (C/mol), $j_0$ is exchange current density (A/m$^2$), $C$ is the reference concentration at which the bulk concentrations of oxidizing and reducing agents are equal (mol/m$^3$), $C_i$ is the concentration at the electrode surface of species $i$ (mol/m$^3$), $i$ is either Ox or Red, $a$ is the charge transfer coefficient, $k^0$ is the standard heterogeneous rate constant (m/s), $\eta$ is the overpotential (V), $R$ is the gas constant (J/(mol K)) and $T$ absolute temperature (K).[4]

2.2. Thiele modulus
Thiele modulus $\varphi_n$ and the effectiveness factor $\eta$ are simple terms to analyze the catalytic activity and the diffusional resistance of dispersed species in a porous electrode. [13] The lower Thiele modulus leads to better diffusion profile. For each nanostructure, Thiele modulus was derived based on the following equation[9, 10]:

$$ \varphi_n = L \cdot \sqrt{\frac{k}{D}} \tag{3} $$

where

$$ k = k^0 \frac{A_r}{V_D} \tag{4} $$

$L$ is the diffusion distance (m), $D$ is the diffusion coefficient (m$^2$/s), $V_D$ is the volume available for diffusion of molecules (m$^3$), and $A_r$ is the area of the surface of reaction (m$^2$). Likewise, the effectiveness factor is defined in the following equation:
\[ \eta = \frac{\tanh(\varphi_n)}{\varphi_n} \]  

(5)

2.3. Simulation software

Finite element simulator COMSOL Multiphysics® was used for studying and comparing the catalytic activity of the proposed external hierarchical nanostructures. The catalytic activity was investigated in 2D simulation model after mapping the diffusion coefficient from 3D simulation model.

2.4. Geometry of nanostructures

The geometry of investigated nanostructures is shown in figure 1. The hierarchical nanostructure contains one macrostructure (gray) and many nanowires with a variable length \( L \) as microstructure (black). The length of nanowires and the diameter of the macrostructure adjust \( R_f \). The length of nanowires was set during the simulation to 200 nm, 500 nm and 1000 nm.

In figure 1, the gray and black colors represent the solid-phase and the blue color represents the void-phase. The reaction surface, at which the oxidation of methanol takes place, is the outer surface of the solid phase. Each \( R_f \) and each \( L \) had a stand-alone 2D component in one simulation file. In each component, one nanostructure was placed at the bottom of a rectangular simulation model of width 20 µm and height 10 µm. Moreover, the top edge of the rectangle was set as an inflow boundary condition, the side edges were set as symmetry boundaries, and the bottom edge was set as a wall.

![Figure 1. The model of half-cell of DMFC and boundary conditions of simulation.](image)

![Figure 2. Diffusion constant from 3D to 2D mapping.](image)

3. Results and discussion

3.1. Diffusion coefficient mapping

Because of computational limitations in 3D models, 2D simulation models were chosen to investigate the catalytic efficiency of proposed geometries and variations. Unfortunately, there is no 2D cross-section that achieves symmetry in the 3D geometry. Therefore, it was not possible to map the results of 2D model to the results of 3D model based on geometrical aspects. Thus, specific activity was considered as a mapping criterion because it involves the average rate of mass transport of active species to the active sites and the average molecule turnover rate at each active site. Figure 2 shows the specific activity of 2D and 3D simple external non-hierarchical nanostructures (not shown in this paper) in a wide range of diffusion coefficients. Considering the diffusion coefficient of methanol \( D_{\text{meth}} = 0.84e^{-9} \) m²/s [14], the equivalent diffusion coefficient of methanol in 2D for the equivalent specific activity is \( D'_{\text{meth}} = 5e^{-9} \) m²/s. The found value of \( D'_{\text{meth}} \) was used for all simulations in this paper.
3.2. Kinetics of external hierarchical nanostructures

The specific activity, as shown in figure 3, is inversely proportional to the length of nanowires. Additionally, specific activity is also inversely proportional to $Rf$ of surface. Therefore, when the nanostructures achieve an equal $Rf$ of surface, the one with shorter nanowires length features higher specific activity. Moreover, the specific activity is related to the concentration at the direct vicinity of nanostructures surface because both quantities are influenced by molecules turnover rate at surface and mass transport rate to active sites. However, the current density is directly proportional to $Rf$ at all nanowires lengths (figure 4). Only a slight deviation in the curve of $L = 1000$ nm at higher $Rf$ is observed. The shorter nanowires show larger current density, especially at high $Rf$ values. Unlike the specific activity, although the average turnover rate decreases at high $Rf$, the number of catalytic active sites increases and therefore the total turnover of molecules increases, which results in a larger current density. It is import to note, even though the shorter nanowires at specific $Rf$ address higher total turnover, the high $Rf$ values are only achieved by long nanowires.

**Figure 3.** Specific activity of different nanowires length with respect to the surface roughness factor.

**Figure 4.** Current density of different nanowires length with respect to the surface roughness factor.

**Figure 5.** Thiele modulus of different nanowires length with respect to the surface roughness factor.

**Figure 6.** Effectiveness factor of different nanowires length with respect to the surface roughness factor.

The current densities (figure 4) in case of $L = 200$ nm and $500$ nm with respect to $Rf$ are more identical compared to the current density in case of $L = 1000$ nm because of the kinetics regime. According to Thiele modulus (figure 5), the kinetic regime in case of $L = 1000$ nm is limited by
diffusion, while there are no mass-transport limitations due to diffusion when \( L = 500 \text{ nm and 200 nm.} \) The catalytic efficiency (figure 6) for \( L = 1000 \text{ nm drops to 50\% at } R_f = 140, \) whereas the high efficiency with no mass-transport limitation is achieved by the shorter nanowires. When \( L = 200 \text{ nm,} \) the effectiveness factor is close to 1, which means perfect mass transport to all active sites regardless the value of \( R_f. \) Likewise, when \( L = 500 \text{ nm, the kinetic regime stays at k-controlled region and high mass transport efficiency is achieved. Therefore, increasing } R_f \text{ within the simulation range, results in increasing the total catalytic activity but simultaneously decreasing the specific activity because of decreasing in pore accessibility and catalytic efficiency of nanostructures.}

4. Conclusions
Our investigations showed that 3D simulation and 2D simulation of external hierarchical nanostructures are asymmetrical. Therefore, the variation in 3D catalytic activity was compensated by the diffusion coefficient in 2D simulations, which delivered the specific activity of methanol in 3D simulations. It was shown that specific activity was inversely proportional to the length of the nanowires and \( R_f \) of the surface. This inverse proportion was a result of pore accessibility, which was confirmed by calculating Thiele modulus and effectiveness factor. The nanostructures with longer nanowires and their higher density resulted in lower pore accessibility as well as lower specific activity because of larger diffusional resistance. It was determined that in the simulated \( R_f \) range, the nanostructures with nanowires having \( L = 200 \text{ nm and 500 nm showed a kinetic controlled regime,} \) while the nanostructures, which have nanowires with \( L = 1000 \text{ nm, showed diffusion controlled regimes. Nevertheless, the number of the catalytic actives sites increased at large values of } R_f. \) Therefore, it was confirmed that the current density increased by enlarging the surface roughness.

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