



Mass transport and catalytic activity in hierarchical/non-hierarchical and internal/external nanostructures: A novel comparison using 3D simulation



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ABSTRACT

The distinct organization of nanostructured materials influences several catalytic characteristics, like selectivity, sensitivity or catalytic efficiency. This paper studies the effect of geometrical configuration of nanostructured catalyst on mass transport and catalytic activity based on 3D simulations of hierarchical external, hierarchical internal, non-hierarchical external and non-hierarchical internal nanostructures. Generally, external nanostructures revealed higher utilization of catalytic surface than the internal nanostructures. Among the four investigated nanostructures, the mass transport in hierarchical external nanostructures was found to be the best; they even showed kinetic controlled regime for the species with low diffusion coefficient. In contrast, hierarchical internal nanostructures showed slightly less specific activity than non-hierarchical internal nanostructures because of higher total diffusional resistance and longer diffusional path. As a result, although hierarchical nanostructures possess large surface area, only the hierarchical external nanostructures provided an outstanding accessibility of active sites. The obtained results provide the tool for understanding the catalytic efficiency in complex nanostructure and phenomena that are technically difficult to measure.

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1. Introduction

Applications of nanoporous electrodes in electrochemical devices, like fuel cells [1,2], supercapacitors [3], batteries [4], glucose sensors [5], etc., have become a significant growing field during last decades. In the field of catalytic reactions, nanoporous electrodes have gained the significance because of their high surface-to-volume ratio, which results in high catalytic surface area [6,7]. The total catalytic surface area can be influenced by roughness factor (Rf), which is defined as the ratio between the total nanoscopic catalytic surface area and the geometrical surface area [8]. There are a large number of nanostructures that have been reported for several catalytic reactions. Therefore, tuning the nanostructures to a specific catalytic reaction and optimizing the catalytic activity are of great importance, because the identification of an optimal nanostructure is still a great challenge [9]. Catalytic activity is proportional to reaction rate, which is defined by the

number of molecules that get catalyzed per second. Thus, catalytic activity depends on the number of active sites and on the average rate of molecules turnover at active sites [10–12]. Besides the chemical characteristics, morphology of nanostructures plays a key role in the catalytic performance because of its influence on the accessibility of the active sites [13]. The pore-size is thereby a key factor for the determination of pore accessibility due to its impact on diffusion resistance. Based on pore-size, the porous material is described as either microporous (<2 nm), mesoporous (2–50 nm), or macroporous (>50 nm) [14,15]. Recently, many synthesis processes associated with protocols for pore morphology adjustment were reported, for example, alloying/dealloying process [16,17], annealing process [18,19], templating method [20], pulsed electrodeposition [21], and cyclic electrodeposition [22].

The nanostructures can be classified based on their morphology into non-hierarchical nanostructures, also called 1D nanostructures, like nanowires [23], nanorods [24], and nanotubes [25], or hierarchical nanostructures, also called 3D nanostructures, such as flower-like [26], spherical nanostructures [27], nanopropeller-shaped [28], nanorings [29], and nanohelices [30]. Non-hierarchical nanostructures are composed of one level or one direction of the catalytic surface area, whereas hierarchical nanostructures are composed of macro- and micro-/mesostructures, which are

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assembled in more than one dimension [24,31]. In 1998, Yang et al. reported the first hierarchical porous nanostructures. These nanostructures were adjustable from 10 nm to several micrometers [32]. Currently, there are several synthesis procedures for hierarchical nanostructures; they can be synthesized either by non-template methods by self-assembly of crystallites [31] or by template method [20,31] using hard/soft templates or bio-molecules foams.

The diffusion of reactants inside porous nanostructures is influenced by the geometry of pores. In non-hierarchical nanostructures, the reactant molecules suffer from the high mass transfer resistance inside the pores, and in consequence the molecules were restrained from reaching some active sites [9]. Pore accessibility can be increased by using 3D interconnected pores because of the enhancement of the diffusion of fuel molecules [31]. Therefore, hierarchical nanostructures, which can enhance the accessibility of active sites, are considered as candidates for optimizing the mass-transport limitations in non-hierarchical nanostructures and for enhancing the catalytic activity for the desired reaction [9,31,33]. Thus, hierarchical nanostructures are the best candidates for catalytic applications with slow kinetics [34]. Additionally, the hierarchical nanostructures are well-employed in nature, lungs and kidneys are examples of improving the diffusion of slow diffusive nutrients and oxygen in a network of vessels [35]. However, hierarchical nanostructures are expensive due to the high metal usage [36].

Modelling of mass transport and catalytic efficiency of porous layers, including hierarchical nanostructures, was carried out by several groups [37–41]. Many groups optimized the catalytic activity of porous layers by introducing a distributor channel (macropore) that interconnects the meso-/micropores, i.e., porous layer of hierarchical nanostructures [42–46]. The significant macropore characteristics are the distributor geometry [43], volume fraction [43–46], pore-size [44,45], and the optimal link between macropores and meso-/micropores [43,47–49]. For example, Coppens and coworkers found that, in gases, the diffusion in macropores is the only limitation of the pores kinetics [46], but small pores are also significant in gas conversion simply because of the multitude of small pores [35].

In this paper, we investigate four configurations of porous layer, hierarchical and non-hierarchical of external and internal nanostructures, by means of 3D simulation in order to study the effect of the morphology on catalytic activity. These geometries are based on experimental investigations of external nanostructures [23]. The 3D simulation was used to overcome the symmetry limitations of hierarchical nanostructures, and to provide a general and more realistic model that estimates catalytic activity of any nanostructures geometry. We considered, as illustrated in Fig. 1, vertical grown cylindrical nanowires for non-hierarchical external nanostructures (N-Ex) (Fig. 1a) and a sea-urchin nanostructure for hierarchical external nanostructures (H-Ex) (Fig. 1c). For investigation of internal nanostructures, we chose two previously reported geometries that are analogous to the imprint of our external nanostructures, especially in relation to the equivalent geometrical parameters, like R_f and surface area, for the purpose of comparison. The nanostructures with vertical cylindrical holes [47,50] was considered for non-hierarchical internal nanostructures (N-In) (Fig. 1b) and the imprint of a sea-urchin nanostructures that contains macropores as distributor channels to micro-/mesostructures [42,46,51] was considered for hierarchical internal nanostructures (H-In) (Fig. 1d).

Unlike the investigations reported in literature, the main goal of this paper is the investigation and comparison of the reaction kinetics on several proposed nanostructures based on their morphology because of the expected dissimilar mechanisms of mass transport inside these geometries. In this paper, a model system

that combines the electrocatalytic and mass transport behaviors is applied. Thus, it provides fundamental understanding of the catalytic activity based on molecules diffusion and kinetic parameters. Furthermore, the study was extended to the investigations of diffusional resistance inside each porous structure through Thiele modulus and the effectiveness factor. Further evaluations of the migration of protons resulting from the oxidation process were carried out by consideration of pH-value at the direct vicinity of the porous electrode [23]. Nevertheless, some factors that influence kinetic parameters, like adsorption and temperature [52–54] as well as the electrolyte conductivity and the associated influence of potential on ions migration were not considered within the scope of this paper.

2. Methods

2.1. Reaction kinetics

The reaction kinetics at the anode was investigated in our simulations by considering an arbitrary organic fuel as a reducing agent (Red). Eq. (1) represents the oxidation process occurring at the anode [55]:



The kinetics of the reactions occurring on the electrode surface is influenced by the electrode potential [56,57]. The current-potential characteristics were determined according to Butler–Volmer equation which predicts the currents resulting from the overpotential on the electrode [57]:

$$j = \frac{j_0}{C} \left[C_{\text{Ox}} \exp\left(\frac{-\alpha F \eta}{RT}\right) - C_{\text{Red}} \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) \right] \quad (2)$$

with

$$j_0 = F k^0 C_{\text{Ox}}^{1-\alpha} C_{\text{Red}}^{\alpha} = F k^0 C \quad (3)$$

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 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, α is the charge transfer coefficient, k^0 is the standard heterogeneous rate constant (m/s), η is the overpotential (V), R is the gas constant ($\text{J}/(\text{mol K})$) and T absolute temperature (K) [56].

2.2. Mass transport

The mass transport of corresponding species, i.e., reducing agent (fuel) or oxidizing agent (protons), was only derived by diffusion and no convection mass transport was exerted at any of simulation boundary conditions in this paper. Therefore, isotropic diffusive mass transport was modeled according to the Fick's equation which is a built-in equation of COMSOL [58]:

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i \quad (4)$$

where \mathbf{N}_i represents the flux per unit area, i.e., the number of moles of substances i per unit of time per unit of area ($\text{mol}/(\text{m}^2 \text{s})$), D_i is the diffusion coefficient, \mathbf{u} is the field velocity, and c_i is the concentration of i (mol/m^3) [59]. Since there was no convection transfer, the velocity field $\mathbf{u} = 0 \text{ m/s}$. Therefore, Eq. (4) were simplified to:

$$\mathbf{N}_i = -D_i \nabla c_i \quad (5)$$

2.3. Thiele modulus

To study the impact of nanostructures morphology on the catalytic efficiency of the electrode based on the diffusion of fuel

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