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Dealloying of platinum-based alloy catalysts: Kinetic Monte Carlo simulations

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ABSTRACT

Kinetic Monte Carlo simulations are performed to study the dealloying of Pt-based nanoparticles typically used as oxygen reduction reaction catalysts. The Kirkendall effect is represented to emulate the synthesis of hollow nanoparticles by removing the Ni core in a Ni-core/Pt-shell nanoparticle. It is found that initial shell vacancies are required to completely dissolve the non-noble core. The evolution of porosity is followed by dealloying $Ni_{0.75}Pt_{0.25}$ and $Co_{0.63}Pt_{0.37}$ nanoparticles. Two critical potentials define regions where the bimetallic particles may exist as core–shell, porous, and hollow structures, accompanied with clear variations in the dissolution rates. The phenomena are characterized by the dynamic evolution of the surface coordination numbers, and that of the surface area per platinum mass.

1. Introduction

Dealloying is the selective removal of elements from an alloy. According to recent experimental reports, dealloying that takes place during synthesis of oxygen reduction reaction (ORR) catalysts may yield remarkable activity enhancement by creating characteristic porous or hollow structures [1–6]. However, the dealloying process that occurs during fuel cell operation is enhanced by the concomitant presence of oxygen that promotes metal dissolution and causes the degradation of the catalyst. Therefore, it is crucial to understand the dealloying mechanism in order to use it for tailoring the synthesis of improved catalysts and to prevent the degradation of such catalysts under operating conditions.

Several theoretical studies have demonstrated the usefulness of coarse-grained approaches such as kinetic Monte Carlo (KMC) simulations for the molecular understanding of processes taking place in relatively long time scales, comparable to experiments [7–12]. Here we study the driving forces and the effect of dealloying on the structure of alloy nanocatalysts during their synthesis using KMC simulations. The KMC method requires the correct representation of all the relevant processes in the system in the form of rate expressions. The algorithm selects the processes taking place at each time step based on the magnitude of their rates within a random approach. We present the results of a 3D simulation code capable of studying the degradation and dealloying processes in ORR nanocatalysts including the environmental effects of the electrolyte. Two cases of study are reported here: the synthesis of hollow nanoparticles resulting from removal of the alloy core through dealloying using the Kirkendall effect, and the synthesis of porous nanoparticles by selective dealloying of the less-noble component. Both cases are relevant for improving the understanding of the possible structures of state-of-the-art ORR catalysts.

2. Computational details

The initial configuration of the system in the KMC model consists of a nanoparticle with a FCC structure surrounded by electrolyte particles as depicted in Fig. 1a. For the Kirkendall effect simulations (Fig. 1b) either pure or bi-metallic core/shell systems with and without vacancies in the shell were considered. For the evolution of porosity simulations, $Ni_{0.75}Pt_{0.25}$ and $Co_{0.63}Pt_{0.37}$ nanoparticles with an initial radius between 25 and 40 Å were studied.

All the species occupy a site in the 3D simulation lattice and they may participate in two reactions: diffusion and dissolution. The rate $k_{p,i}$ for the reaction p involving site i is calculated with Eq. (1), where $A_{p,i}$ is the prefactor in sites/s, $E_{B,i}$ is the total bonding energy, given by Eq. (2), which depends on the number of nearest neighbor sites of type n_j and the pair bonding energy parameter $E_{b,ij}$ (Eq. (3)); $\alpha_{p,i}$ is the transfer coefficient parameter, E is the applied potential, $E_{0p,i}$ is the reference potential, T is the temperature, and k_B is the Boltzmann constant.

$$k_{p,i} = A_{p,i} \exp\left[-\frac{E_{B,i} + \alpha_{p,i}(E - E_{0p,i})}{k_B T}\right] \quad (1)$$

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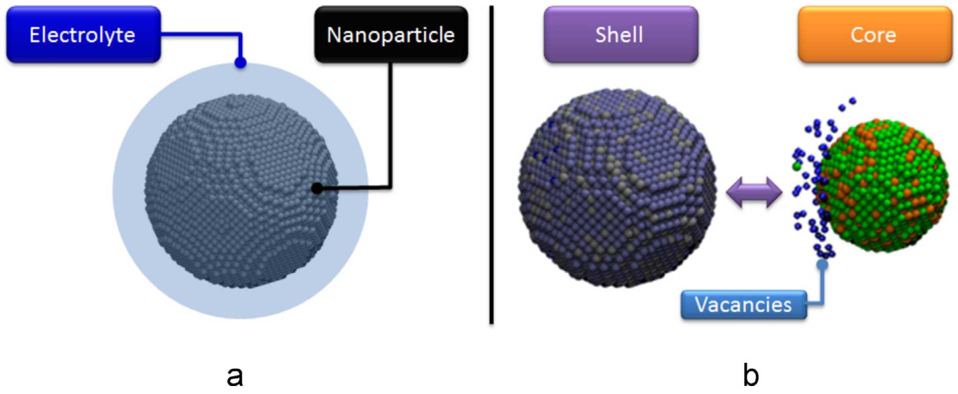

Fig. 1. Examples of initial configurations for the KMC simulations. (a) Schematic representation of the electrolyte lattice sites surrounding the nanoparticle. (b) Multi-metallic systems were considered for the Kirkendall effect simulations, an amount of vacancies were placed in the shell in some cases (see Section 3 in the text).

$$E_{B,i} = \sum_{j}^{\text{Neighbors}} n_j E_{b,ij} \tag{2}$$

$$E_{b,ij} = \frac{E_{b,ii} + E_{b,jj}}{2} \tag{3}$$

Provided the value of the transfer coefficient $\alpha_{p,i}$, the processes may depend on the applied potential. The bonding energy parameters for pure species $E_{b,ii}$ were calculated from density functional theory (DFT) simulations as the change in the total energy of a (1 1 1) slab caused by removal of an atom from the subsurface layers divided by the coordination number (12 in the FCC structure). The corresponding bonding parameters for various pure metals are presented in Table 1.

The bonding parameters between Pt and the electrolyte were tuned through KMC simulations using the surface diffusion coefficient obtained from experiments [13], and it is regarded as independent of the applied potential. The effect of the Pt—H_2O bonding parameter on the surface diffusion is shown in Fig. 2. An average diffusion coefficient of 4.70×10^{-19} cm^2/s corresponds to a solution of 1 M $HClO_4$ [13] and a Pt—H_2O bonding parameter of 0.384 eV. Using this approach, different electrolytes may be studied by varying the metal–electrolyte bonding parameter. However, in the results reported here a constant value of 0.384 eV was used for all the metals considered.

The two processes that are allowed to occur in these KMC simulations are diffusion and dissolution, and they are expressed by Eqs. (4) and (5), respectively. In the diffusion process two species in neighbor sites exchange coordinates, whereas in the dissolution process a metal site is substituted by an electrolyte site.

$$\text{Diffusion}: \begin{array}{l} \text{species}_1 \text{ at site } i \rightarrow \text{species}_1 \text{ at site } j \\ \text{species}_2 \text{ at site } j \rightarrow \text{species}_2 \text{ at site } i \end{array} \tag{4}$$

$$\text{Dissolution}: \quad \text{metal at site } i \rightarrow \text{electrolyte at site } i \tag{5}$$

Table 1
DFT calculated bonding parameters for pure metals used in KMC simulations.

Atom *i*	Bonding parameter $E_{b,ii}$ (eV)
Pt	0.529
Pd	0.524
Co	0.777
Ni	0.571
Cu	0.382
Rh	0.746
Ir	0.856
Ag	0.285
Au	0.294

The selected KMC algorithm was the First-Reaction method [14] (FRM) which is able to simulate processes with time-dependent rates required for the variable potential studies presented in the next sections. The FRM has been successfully applied to simulate temperature programmed adsorption and reaction of O_2 on Pt(1 1 1) surfaces [15]. The flow diagram of a KMC simulation using the FRM is presented in Fig. 3. The required random number generator that picks a process for evaluation at each simulation step was the Maximally Equidistributed Combined Tausworthe generator by L'Ecuyer [16,17].

An inherent practical issue of the KMC method arises when the studied processes have very different time scales, that is, one process is much faster than the others. These fast processes occur in most of the simulation steps, especially using the FRM. Therefore, they consume practically all of the computer time without allowing other processes to occur; although they may be possible, but they have a much lower rate. This problem typically occurs at the nanoparticle-electrolyte interface when diffusion is included in the model, as it is in this study. The practical solution to this issue is reducing the diffusion rate to make it comparable to that of the other processes [18,19]. This approach can be justified observing that diffusion occurs so fast that it equilibrates the surface before another process has occurred. Thus, the precise rate of diffusion

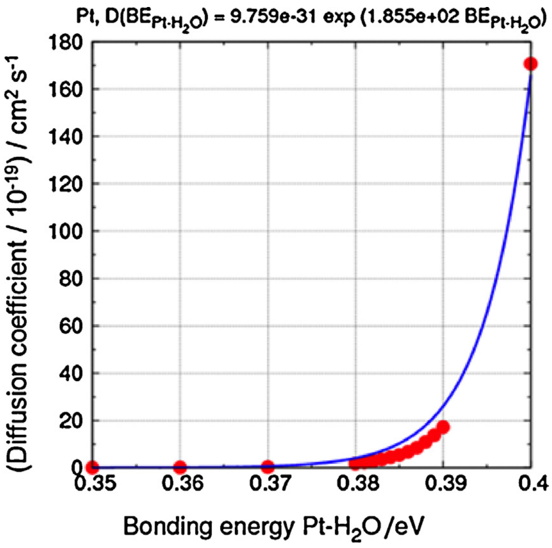

Fig. 2. Effect of the Pt—H_2O bonding parameter on the surface diffusion of a 40 Å radius nanoparticle. KMC simulation results shown as dots and corresponding fitting equation in solid line.