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Full length article

Extent of dissolution determines the structural similarity between dealloyed nanoporous materials synthesized at unrelated dissolution conditions

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ABSTRACT

Most experimental studies on synthesis of nanoporous structures via selective dissolution of electroactive species in metal-alloy nanomaterials report the conditions and the time required to achieve nanoporosity. Depending on the dissolution conditions the timescales of nanoporosity evolution can vary over several orders from sub-second timescales to days, and as such evolution for each condition may appear unrelated. We show that the extent of dissolution (EOD), i.e., the fraction of electroactive atoms dissolved, and not time, is an appropriate descriptor for nanoporosity evolution. Using kinetic Monte Carlo simulations we demonstrate that morphological features obtained over a wide range of temperature, alloy composition, material interactions, etchant concentration and overpotential values are nearly identical for a given EOD. Timescales for different conditions are related by a scaling parameter. Dissolution behavior observed with one experiment can be used to predict results for another experiment, e.g., we relate linear sweep and potential step to constant potential experiments on the basis of EOD. This understanding may be useful for predicting morphology for slow etching/corrosion/leaching conditions from accelerated dissolution experiments as well as design of nanoporous materials.

1. Introduction

Nanoporous metal alloys synthesized via selective dissolution of the electroactive metal is rapidly gaining attractiveness due to the potential applications of these materials in areas of catalysis, battery, supercapacitor and templates [1–3]. Length scale evolution has been carefully investigated in nanoporous AgAu [4–7], NiPt [8–10], PtFe [11,12], PtCo [13], PtCu [9,14,15], AgCu [16], AuCu [17,18], AlAu [19] and PtPd [20] in an attempt to synthesize high-porosity and high-specific surface area materials. Most studies involve tweaking parameters including dissolution time, temperature, alloy composition [21,22], material interactions [23], electrolyte composition [11], size [4,23] and applied potential [4,23] often one-at-a-time to uncover their effect on the nanoporous morphology. Despite this a complete understanding of the length and timescales associated with nanoporosity evolution [24–26], which is essential for nanomaterial design/control, is still crucially missing.

It will be greatly beneficial if morphological features such as surface area can be quickly estimated over a wide range of dissolution conditions from limited experimental data. This capability may allow one to predict slow leaching or corrosion from accelerated dissolution experiments, or estimate conditions where higher surface area or more porous structures can be achieved. Making such extrapolations is challenging as the morphological evolution proceeds in several stages [24–26]. Timescales for each stage are condition-dependent. As a result, the dissolution rates can vary over orders-of-magnitude. Our understanding of the coupling between the process parameters at each stage is also inadequate. For instance, predicting changes in surface area is non-intuitive when the dissolution time and alloy composition are modified together as part of the synthesis protocol. Keeping these challenges in mind, we develop a general procedure to relate nanoporosity evolution for various dissolution conditions.

When the dissolution rate constant is fast in comparison to surface diffusion and complete porous nanostructures are obtained, dissolution can be found to proceed through the same set of stages irrespective of the conditions. Creation of roughness is witnessed at the early stages of nanoporous dissolution. This is followed by the

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formation of a core-shell structure where the core is intact and the shell is porous at the intermediate timescales. The core shrinks as dissolution proceeds. Eventually, a complete porous structure is obtained at longer timescales. Our previous molecular simulation studies indicate that several length scale features such as facet area and ligament diameters may have characteristic values associated with the stages albeit the timescale to reach these stages may vary with condition [27]. We study the advantage of employing the extent of dissolution (EOD), i.e., the fraction of electroactive (EA) species still present in the material, to follow the progression of stages and length/time scales. The EOD is related to the amount of charge transferred for dissolving the reactive species. The total charge transferred is a sum of the amount involved in chemical reactions (dissolution, oxidation, side reactions, etc.) and charging of the electrode-solution interface.

In this work, we show that morphological features for two conditions are found to be nearly identical for the same EOD. Small deviations in the morphology can be observed as conditions are varied. These deviations are captured using the response surface methodology [28]. A response surface model indicates the sensitivity of the morphological features to each experimental parameter and correlations between parameters. Here we explore the effect of temperature, overpotential, alloy composition, binding between metal species and nanoparticle size. Contrary to the usual approach of studying length scale as function of time, we study length-and time-scales as a function of EOD. Response surfaces are generated for dissolution time, (100) and (111)-oriented facets of the nanoporous material for constant potential experiments. An important extension of this understanding is relating different potential experiments. We show that it is possible to relate dissolution time-versus-EOD and surface area-versus-EOD curves obtained for constant potential to ones obtained for time-dependent potential, e.g., linear sweep and potential step experiments. Once nearly complete dissolution of the electroactive species is achieved nanoporosity evolution proceeds mainly via coarsening of ligaments and EOD ceases to be an appropriate variable to follow the evolution.

We employ a kinetic Monte Carlo (KMC) model to illustrate our approach. In KMC, the atoms reside on lattice sites and are allowed to undergo diffusion and dissolution events by selecting events randomly with a probability proportional to the rate constant of the event [29]. Approximate KMC models have been used extensively for more than a decade to understand nanoporous structural evolution with atomistic resolution [26]. The structural evolution using KMC resembles that of the experimental system as long as the rates in the KMC model are accurate. Parameters, such as temperature, overpotential, alloy composition, binding, size, etc., that are known to influence the dynamics can be explicitly included in the model. We restrict ourselves to conditions where full porosity is observed for all conditions, i.e., far from critical potential and parting limit.

The main sections of the paper are as follows. The computational procedure is outlined in Section 2. Results from different potential experiments, response surface modeling, effect of various experimental parameters as well as size effects on porosity, and universality observed during dissolution is discussed in Section 3. Finally, conclusions are presented in Section 4.

2. Computational methodology

2.1. Kinetic Monte Carlo model

A truncated octahedron nanoparticle (NP) consisting of a random alloy A_xB_{1-x} is considered (see left of Fig. 1). Most of our simulations involve 18 nm NP, although, other sizes of 9, 27 and 36 nm have also been considered. The truncated octahedron is chosen because of its lower surface energy compared to other structures. A and B are the electrochemically noble (EN) and electroactive (EA) species, respectively. It is assumed that the alloy adopts a face-centered cubic lattice structure. A and B are miscible and form a random alloy like Au-Ag [30]. Furthermore, no mass transfer limitations are present at the electrolyte side.

The selective dissolution process is simulated using a standard KMC model at a constant temperature [24,27]. In the model, diffusion proceeds via hopping of an atom to its nearest neighbor vacant site. Both EA and EN atoms can participate in hopping events, whereas only EA atoms can be dissolved. The rate constant for hopping is given by

$$k_{diffusion} = \nu_{diffusion} \exp\left(-\frac{\varepsilon_0 + N\varepsilon}{k_B T}\right) \tag{1}$$

Here $\nu_{diffusion}$ is the diffusion pre-exponential factor, N is the number of nearest neighbors, ε is the bond energy, k_B is the Boltzmann constant and T is the absolute temperature. The

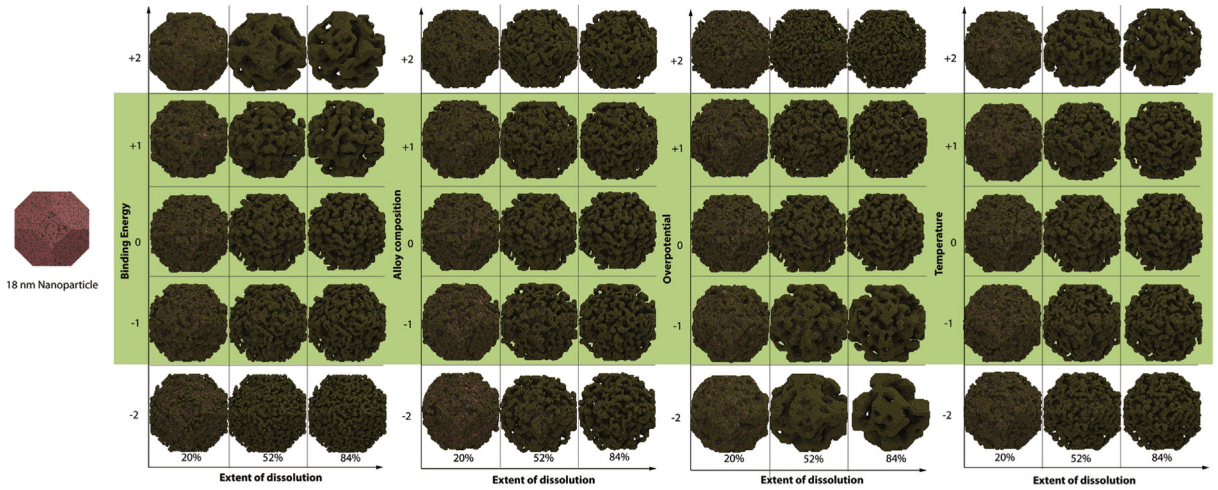

Fig. 1. Evolution of an 18 nm nanoparticle followed in terms of extent of dissolution. Green and pink atoms denote electrochemically noble and active species, respectively. Response surface fits are made only to the shaded green region (levels -1 to $+1$), but are used to predict the behavior for conditions not included in the fit. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)