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Nanoelectrochemistry in electrochemical phase transition reactions

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Electrochemical phase transition is important in a range of processes, including gas generation in fuel cells and electrolyzers, as well as in electrodeposition in battery and metal production. Nucleation is the first step in these phase transition reactions. A deep understanding of the kinetics, and mechanism of the nucleation and the structure of the nuclei and nucleation sites is fundamentally important. In this perspective, theories and methods for studying electrochemical nucleation are briefly reviewed, with an emphasis on nanoelectrochemistry and single-entity electrochemistry approaches. Perspectives on open questions and potential future approaches are also discussed.

1. Introduction

Phase transition occurs in various electrochemical reactions that are technologically and industrially important. For example, gas bubbles can form at the electrode surface during gas evolution reactions when the gas species are locally supersaturated near the electrode. Some of the important reactions include the chlorine evolution reaction (CER) in the chloralkaline process, as well as the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water electrolysis. The bubbles can block active sites on the electrode, creating additional overpotential and energy loss in the electrolysis. On the other hand, the detachment and motion of bubbles can create convection and enhance mass transfer in electrocatalysis. The evolution of bubbles in electrochemical reactions has been reviewed recently.[1,2] Electrochemical formation of a new solid phase, often known as electro-crystallization when the solid is crystalline, is also fundamentally important in aluminum production, electroplating, as well as in batteries based on metal anodes.[3–6]

Electrochemical phase transition often needs nucleation to be the first step. Nucleation describes the clustering of ions, atoms, or molecules *via* fluctuation to form an assembly of a critical size before the further growth of the new phase is energetically favorable. Therefore, the kinetics and mechanisms of nucleation at electrochemical interfaces can greatly impact many electrochemical processes involving phase transition. For example, designing an electrochemical interface that induces smooth nucleation and growth is key to developing safer batteries.[7,8] Tuning the nucleation behavior to better manage bubbles in electrocatalytic gas evolution reactions can increase the efficiency of electrolyzers.[9]

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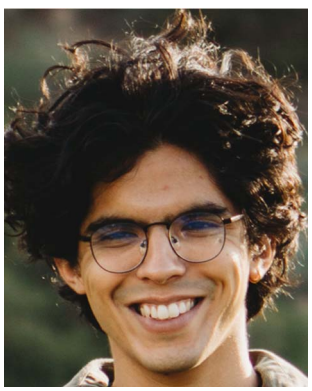

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In this perspective, we focus on the nucleation process in the electrochemical phase transition. The readers are referred to other relevant papers for other related processes, *e.g.*, growth, aggregation, and Ostwald ripening.[10–15] We will first introduce the theories and models in electrochemical nucleation. Some experimental methods to study the nucleation of solids and gas bubbles at electrochemical interfaces will then be highlighted, with an emphasis on nanoscale electrochemical methods. Finally, open questions and perspectives on future directions in studying electrochemical nucleation will be provided.

2. Nucleation theories in the electrochemical phase transition

Several general nucleation theories have been developed, which can be used to understand and analyze the experimental results in electrochemical nucleation to reveal mechanistic insight. Here, we will primarily focus on classical nucleation theory, which forms the basis for many other theories. The atomistic nucleation model and non-classical nucleation model will also be discussed.

2.1 Classical nucleation theory (CNT)

First developed by Volmer, Weber,[16] and Zeldovich,[17] CNT is a continuum theory describing the energetics and kinetics of nucleation, which has been successfully applied in electrochemical phase transition processes. According to CNT, forming a new phase requires overcoming an activation barrier determined by the cluster of a critical size called the critical nucleus. This critical nucleus results from the competition between the volume energy for forming a new phase and the interfacial energy for forming a new surface (Fig. 1a). CNT predicts the rate of nucleation as:

$$J = J_0 \exp\left(-\frac{16\pi\gamma^3\Phi(\theta)}{3k_B T\Delta G_v}\right) \quad (1)$$

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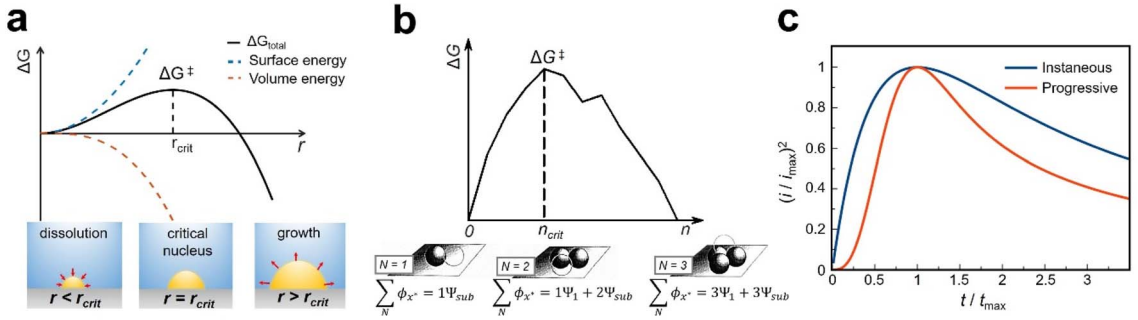

Fig. 1 (a) Free energy in forming a new phase *vs.* size of the new phase showing a barrier at a critical size (r_{crit}) predicted by classical nucleation theory (CNT). Adapted with permission from ref. 35. Copyright 2019 American Chemical Society. (b) Free energy in forming clusters of discrete numbers of atoms in the atomistic nucleation model. Adapted with permission from ref. 25 & 26. (c) Current–time traces predicted by the Scharifker–Hills model showing progressive *vs.* instantaneous nucleation.

In eqn (1), J is the nucleation rate, J_0 is the pre-exponential factor, γ is the interfacial energy of the interface between the electrolyte and the new phase, $\Phi(\theta)$ is a geometric factor related to the shape of the nucleus, k_B is Boltzmann's constant, T is the temperature, and ΔG_v is the volume energy for forming the new phase. In electrochemical nucleation, the driving force is controlled electrochemically. For example, in the electrochemically induced bubble nucleation, the supersaturation ratio of gas at the electrode can be controlled by the current of the gas evolution reaction. In electrodeposition, supersaturation is directly controlled by the overpotential. If a 3-dimensional nucleus is assumed in electrodeposition, the nucleation rate can be expressed as

$$J = J_0 \exp\left(-\frac{16\pi\gamma^3 V_a^2 \Phi(\theta)}{3n^2e^2\eta^2 k_B T}\right) \quad (2)$$

In eqn (2), V_a is the atomic volume of the electrodeposited atom, η is the overpotential, n is the number of electrons of the reaction, and e is the elementary charge.[12] If 2-dimensional nucleation is operating, the η^{-2} term in the exponent is replaced with η^{-1}. CNT has been widely used in electrochemical nucleation (*vide infra*), which successfully explains the kinetics of nucleation as a function of supersaturation ratio, as shown in Ag nucleation and bubble nucleation.[18–22] However, because the critical nuclei often contain only a small number of atoms,[23,24] whether macroscopic interfacial energy still holds is debatable.

2.2 Atomistic nucleation model

The atomistic nucleation model, developed by Milchev,[25] describes the formation of nuclei as the addition and removal of individual atoms to clusters (Fig. 1b). This model considers the interactions between individual atoms (binding energy), and individual atoms and the substrate without invoking the macroscopic interfacial energy, leading to a discrete character for the critical nucleus size as opposed to classical nucleation theory (CNT).[26]

2.3 Non-classical nucleation theory

Non-classical nucleation theories have also been proposed to explain some of the observations in phase transitions. Specifically, a two-step nucleation process has been observed in the crystallization of ionic solids: a metastable intermediate phase is first formed, followed by reorganization into an ordered structure.[27,28] These observations are inconsistent with CNT, which predicts a single nucleation step without a metastable intermediate. On the other hand, it has been suggested that even when nucleation involves a multi-step mechanism, the fundamental concepts in CNT still hold.[29]

3. Methods to study electrochemical nucleation

Nucleation at the electrochemical interface can be controlled and measured electrochemically. In electrodeposition, the location of nucleation and the average nucleation rate can be measured by counting the density of the particles formed on the electrode surface after the deposition using SEM or AFM. For example, the nucleation rate during Ag and Pt deposition as a function of potential and their preferential sites on HOPG has been identified using this method.[30,31] *In situ* methods for studying nucleation at the electrochemical interfaces, especially liquid-cell TEM, have also provided structural and morphological information during the formation of a new phase in electrodeposition.[32–34]

3.1 Conventional electrochemical methods

Electrochemical nucleation can perturb the current or potential on the electrode surface, which can be used to probe nucleation. For example, the Scharifker–Hills model allows the measurement of the density of the nucleation site and nucleation rate by analyzing current–time traces at constant potential (Fig. 1c).[35] One prediction is the existence of two extreme cases in nucleation: progressive and instantaneous nucleation, which corresponds to slow nucleation and fast nucleation, respectively, and result in different current–time traces, as shown in Fig. 1c. Other variations, including the inclusion of the non-steady state electrochemical processes and dispersion of nucleation rate, were developed by Fleischmann, Fletcher, and others.[36–38] While the models can be applied to bulk amperometry experiments, the measured nucleation rate is an average over all the activated

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nucleation sites because most bulk electrodes will contain a distribution of different nucleation sites. Information about the heterogeneity of the nucleation sites and their effect on the nucleation rate is lost in averaging.

3.2 Measuring one nucleation event at a time

Budevski and coworkers have pioneered the study of single nucleation events in preparing atomically flat Ag surfaces,[39] which is now classified as single-entity electrochemistry.[40] The complication from multiple competing nucleation events can be mitigated by studying one nucleation event at a time. On these "defect-free" surfaces, nucleation is required before the growth of a new layer is favorable, resulting in the layer-by-layer growth of Ag (Fig. 2a). The induction time for nucleation is used to measure the kinetics of nucleation, which verifies the applicability of CNT in electrodeposition.[20] While this pioneering work is elucidating, the method requires the preparation of an atomically flat, "defect-free" electrode surface over hundreds of microns to millimeters, which has been demonstrated successfully on Ag.

3.3 Nanoelectrochemistry and single-entity electrochemistry

Nanoelectrochemistry has greatly expanded the scope of single nucleation measurement. Instead of preparing a defect-free surface, nanoelectrochemistry approaches involve shrinking the electrode to the nanoscale, reducing the number of active nucleation sites to unity. White and coworkers have demonstrated this principle in the nucleation of single nanobubbles, including H_2, N_2, O_2, and CO_2.[41–44] A typical voltammogram involving the nucleation of a single nanobubble on a nanoelectrode is shown in Fig. 2b: a characteristic peak is observed when a single bubble nucleates and grows at the electrode to block the current. The surface concentration of the dissolved gas molecules and supersaturation ratio can be obtained from this peak current. The supersaturation ratio for bubble nucleation was shown to range from 300 for H_2 to 18 in CO_2, depending on the gas type, while the number of molecules in the critical nucleus is almost unchanged (50–90) regardless of gas type (Fig. 2c).[22,35,44] The same methods can also be applied to study the nucleation of metals, *e.g.*, Hg and Ag, as demonstrated by Mirkin and White, respectively.[45,46] Depending on the theoretical framework, the critical nucleus of Ag on carbon was found to be 1 to 9 atoms for CNT and 1 to 5 atoms using the atomistic model in the overpotential range of −130 to −70 mV.[46] The nucleation of a single ionic solid particle, like $CaCO_3$, has also been studied on a nanoelectrode.[47] Here, supersaturation in terms of the equilibrium of solubility of $CaCO_3$ was induced by electrochemically changing the pH near the electrode. Future work can test the viability of different nucleation theories by evaluating the nucleation rate *vs.* supersaturation and comparing the results with theoretical predictions.[47] Overall, the nanoelectrode method greatly simplifies the interpretation of the nucleation measurements, which provides rich information about nucleation. However, the structure of the nucleation sites on different electrodes is generally difficult to control and characterize. In addition, the electrode materials for making nanodisk electrodes are limited to a few conductors, mainly Pt and Au.

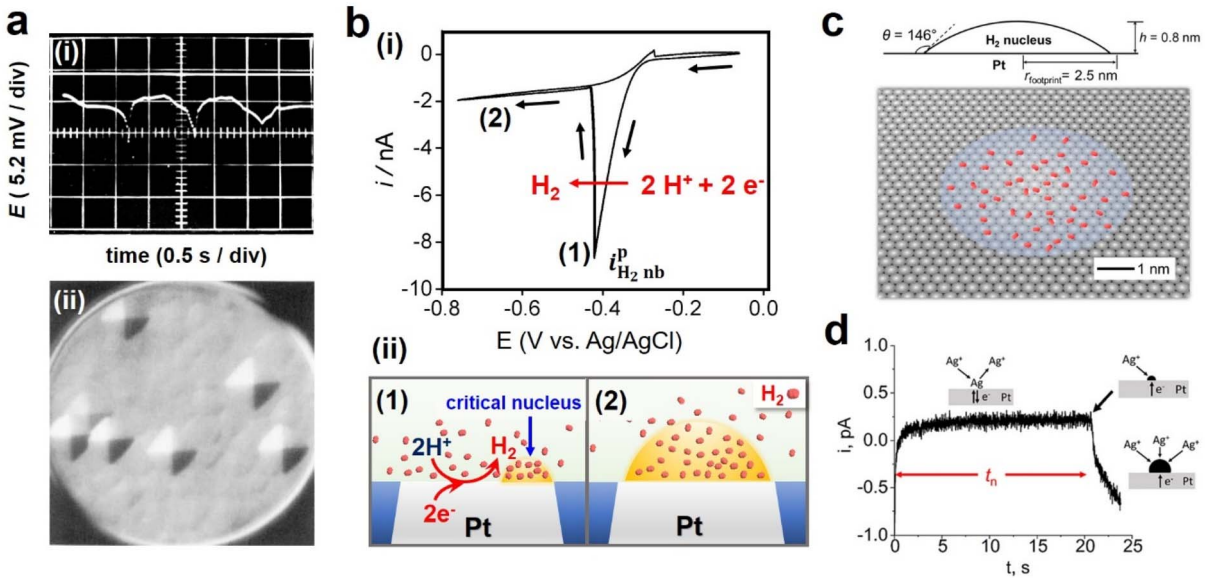

Fig. 2 (a) (i) E–t trace indicating overpotential fluctuation during two-dimensional nucleation of Ag at −65 μA cm^{-2} on a "defect-free" Ag(100) surface and (ii) growth pyramids on the flat Ag(100) plane. Adapted with permission from ref. 19; (b) the nucleation of H_2 nanobubble on a Pt electrode. (i) Cyclic voltammogram, and (ii) schematic illustration of bubble evolution showing (1) critical nucleus and (2) a steady-state H_2 bubble formation at a Pt nanoelectrode. Adapted with permission from ref. 35. Copyright 2019 American Chemical Society. (c) Schematic of the cross-section and 3D view of the critical H_2 nucleus. Adapted with permission from ref. 35. Copyright 2019 American Chemical Society. (d) i–t curve exhibiting the nucleation and the growth of a single Ag nanoparticle on a Pt nanoelectrode. Reprinted with permission from ref. 46. Copyright 2023 American Chemical Society.

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An alternative to the nanoelectrode approach is to use scanning electrochemical probe microscopy methods, especially scanning electrochemical cell microscopy (SECCM). SECCM uses an electrolyte-filled glass capillary with $a < 1$ μm diameter opening, often called nanopipette, to measure local electrochemistry.[48] A combined reference/counter electrode is inserted in the bulk solution side of the nanopipette. The contact between the nanoscopic droplet at the end of the nanopipette and the substrate defines a nanoelectrode as the working electrode, allowing local nanoelectrochemical measurement at different electrode materials. In addition, scanning the nanopipette probe allows electrochemical mapping, and the lateral resolution ranging from a few microns to 30 nm has been reported,[49] depending on the size of the nanopipette, the wettability of the substrate, and the mode of scanning (*e.g.*, lateral hopping distance in the hopping scan). Sub-10 nm diameter nanopipettes have been reported, which promises further improvement in the resolution of SECCM.[50] We have demonstrated mapping the nucleation of H_2 bubbles on polycrystalline Pt using SECCM (Fig. 3a).[51] In this study, we found a heterogeneous distribution of energetics of nucleation for H_2 bubbles which was not correlated with the crystal facets. The fast gas exchange at the droplet–air interface acts as a sink to remove H_2 generated at the electrode surface. As a result, higher currents and higher proton concentrations are needed to induce nucleation compared with those in nanoelectrode experiments. This approach has been applied to study gas bubble nucleation on other substrates and single nanoparticles.[52–54] The results also suggest that when inferring the activity of gas evolution reactions from the current, the possibility of bubble formation that lowers the current should be considered.

Unwin and coworkers have also used SECCM to show that Ag particle nucleation on basal terraces of HOPG involves nucleation, aggregative growth, and detachment mechanism.[55] By comparing macroscale and nanoscale measurements, it was shown that the nucleation site density, calculated using the Scharifker–Hills model, does not agree with the number of particles observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). By SECCM, however, they demonstrated that the disparity in the number of particles was related to a detachment mechanism. This specific mechanism could only be assessed by analyzing nucleation and growth at the nanoscale.

A related nanopipette technique is to induce and study nucleation by controlling the ionic flux in the nanopipette. Siwy and coworkers have demonstrated the formation of ionic precipitates by biasing a potential across nanopores in dilute ionic solutions.[56–59] The precipitates are very unstable and undergo nucleation and re-dissolution, which results in transient blocking and unblocking of the pores that can be observed as oscillations in the ionic current.[58] This opens the possibility of using these nanopores as single-molecule sensors.[56] Unwin and coworkers have shown the synthesis of metal–organic framework (MOF) crystals and other organic crystals with unusual polymorphs (Fig. 3b).[60,61] The ability to apply different voltages across the nanopipette and vary the opening size of the nanopipettes offer possibilities for precise control of crystallization. Wang and coworkers have demonstrated the control of the nucleation and growth of one insulin crystal at the tip of the nanopipette by actively controlling the mass transport within it (Fig. 3c). The simultaneous electrical and optical measurement complements each other in observing the different stages of the crystal nucleation and growth.[62]

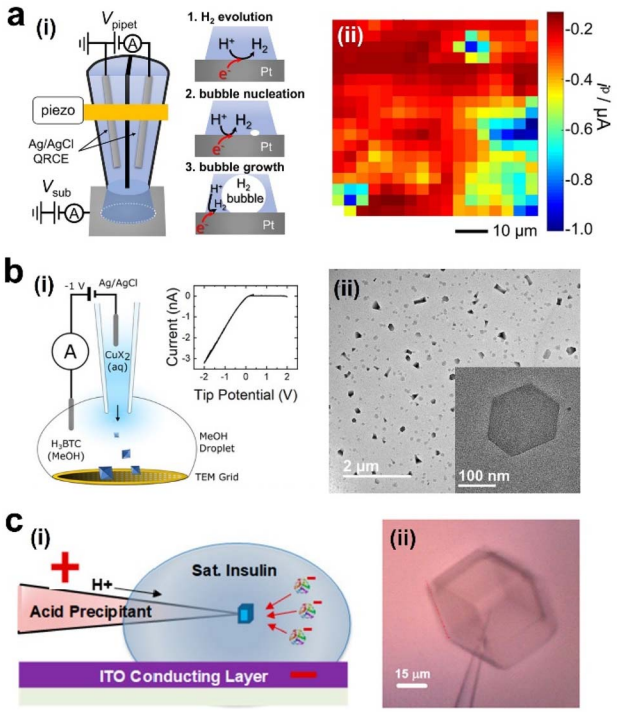

Fig. 3 Nanopipette-based study of nucleation. (a) Left: schematic of mapping the distribution of bubble nucleation on an electrode surface using SECCM. Right: map of nucleation peak current (i^P). Adapted with permission from ref. 49. Copyright 2019 American Chemical Society. (b) Controlled synthesis of metal–organic framework crystals using a nanopipette. (i) Schematic and *i*–*V* curve. (ii) TEM image. Reprinted with permission from ref. 54. (c) Controlled nucleation and growth of a single insulin crystal at the tip of a nanopipette. Left: schematic. Right: an optical image. Reprinted with permission from ref. 56. Copyright 2019 American Chemical Society.

4. Perspectives

Single-entity and nanoelectrochemistry approaches have begun to reveal new information about the kinetics and mechanism of electrochemical nucleation processes. A deeper molecular insight into the nucleation process at the electrode will further positively impact the development of technologically important processes involving phase transition. Below, we summarize our perspectives on electrochemical nucleation studies, including open questions about electrochemical nucleation, and the potential development needed to answer the questions. The open questions include:

(1) What are the molecular and atomic structures of the nucleation sites?

(2) What are the dynamics of the nucleation sites, the nucleus, and the pre-nucleus?

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(3) What are the roles of classical nucleation theory *vs.* non-classical theory in different electrochemical phase transition systems?

(4) How do the interfacial solvent structure and ion distribution affect nucleation?

We believe new analytical methods and measurement tools are needed to address these open questions. It is envisioned that multi-microscopic, spectroscopic, and electrochemical imaging can start to elucidate the nature of the nucleation sites and provide a holistic picture of the nucleation mechanism. Note that these approaches have started to reveal new knowledge about the active sites in electrocatalysis.[40,63–66] In addition, while various analytical techniques have been applied to reveal different aspects of the nucleation, translating these measurements to the conditions relevant to the electrochemical interface, or *in situ*, is needed. Therefore, further development of *in situ* methods with a higher spatial and temporal resolution while minimizing the interference to the electrochemical system is envisioned to test different nucleation mechanisms, *e.g.*, classical, atomistic, and non-classical nucleation theories, and their relevance in different nucleation systems. The high-quality experimental data will in turn help the development of a more refined theoretical framework.[46] For example, *in situ* TEM methods, including the use of graphene membranes, have enabled the imaging of the growth and dissolution of nanoparticles with atomic resolution.[67–69] Combining these approaches with electrochemical control and measurement is promising in revealing the dynamics of the nucleation sites on the electrode surface.[70] In addition, high-speed atomic force microscopy (HS-AFM), which has observed increasing use in imaging the dynamics of proteins and biomolecules,[71] seems suitable to capture the electrochemical nucleation processes *in situ*. Additionally, developing simplified but well-characterized model systems that are amenable to computation study is critical in fully unleashing the power of computation to provide detailed molecular information in electrochemical nucleation processes.[72,73] Moreover, the application of sophisticated statistical analysis, including exploring the spatial and temporal correlation in the data, can reveal hidden mechanisms in complex and high-dimensional data,[35] which have been recently demonstrated in the discovery of non-random nucleation in electrochemical roughening on Pt.[74]

Finally, developing new technology based on the concept of electrochemical phase transition is also expected to gain increasing interest. These include assembling complex structures and nano-devices in electrochemical additive manufacturing,[75,76] and developing analytical sensors using phase transition.[77] In addition, designing interfaces and interphases that control nucleation (*e.g.*, uniform nucleation in batteries, mitigate or re-direct gas bubble nucleation) can benefit from the fundamental understanding of electrochemical nucleation.

Author contributions

All authors contributed equally to the work.

Conflicts of interest

The authors have no conflicts of interest to declare.

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