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Effects of Side Reactions on the Kinetics of Nanoporous Gold Formation Revealed by Real-Time X-ray Scattering during Electrolytic Dealloying

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Abstract: Nanoporous gold (NP-Au) is used in various energy applications. However, little attention has been paid to the nature of surface films which can grow via side reactions during the formation of NP-Au by selective leaching. These films could significantly impact both the kinetics of NP-Au formation by selective leaching, and the performance of this NP-Au in specific energy applications. While it has been reported that complete removal of Ag from a Au-Ag parent alloy by selective leaching is kinetically more sluggish in HClO₄ than in HNO₃, and that the resulting structure size of NP-Au is smaller when formed in HClO₄ compared to HNO₃, these findings were not attributed to the growth of surface film via side reactions during selective leaching. In this work, small-angle and wide-angle X-ray scattering (SAXS and WAXS) are used in real time during NP-Au formation by selective electrolytic leaching of Ag from a Au-Ag parent alloy in 1 M HClO₄ and 1 M HNO₃ to demonstrate that the sluggish dealloying behavior in HClO₄ results from the growth of a surface film during dealloying. In HClO₄, Ag⁺ ions released from the Au-Ag working electrode spontaneously react with Cl⁻ ions released from ClO₄⁻ reduction at the counter electrode to form an insoluble AgCl passive film on NP-Au. The AgCl hinders Ag dissolution and surface diffusion of Au atoms, slowing down the reaction kinetics and the rate of ligament growth. Our findings shed light on dealloying reaction mechanisms and will contribute to better control of the morphology and surface chemical state of nanoporous metals for energy applications.

INTRODUCTION

In the past decades, nanoporous metals have been the subject of intense research, partly owing to their wide range of potential energy applications as heterogenous (electro)catalysts,^{1–3} battery electrodes,^{4,5} supercapacitors,^{6,7} 3D current collectors,⁸ 3D nanocapacitors,⁹ and plasmonic materials.^{10–12} Nanoporous metals are typically created by selectively removing a sacrificial element from a parent alloy using a variety of methods including free corrosion dealloying,¹³ electrolytic dealloying,^{14–16} liquid metal dealloying,¹⁷ vapor phase dealloying,^{18,19} galvanic replacement,²⁰ reduction-induced decomposition,^{21,22} and thermal decomposition.^{18,23} Nanoporous gold (NP-Au), made by selective etching Ag from a Au-Ag parent alloy using free corrosion¹³ or electrolytic^{14,15} dealloying, is the most commonly studied nanoporous metal system. Despite its success in various energy applications, however, the effects of side reactions on both the kinetics of NP-Au formation by electrolytic dealloying, and its resulting morphology are not well-understood.^{14,15,24} It is well-established that during electrochemical processes the electrolyte and the electrode may undergo an irreversible decomposition through side reactions, which can result in the deposition of solid products in the form of a surface film with thickness ranging from a few molecular layers up to a few nanometers at the electrode/electrolyte interface.^{25,26} While many efforts under the umbrella of battery research focus on understanding and controlling these surface films to prevent material loss and stabilize the electrode material (i.e. the solid electrolyte interphase —SEI— layer in lithium-ion and sodium-ion batteries),^{25,26} less attention has been paid to the impact of surface passive films on aqueous electrochemical systems outside of the battery community. For instance, in the case of nanoporous metal formation by dealloying, only a handful of works by Weissmüller and co-workers,¹⁴ deHosson and co-workers,²⁴ and Erlebacher and co-workers,¹⁵ suggest the formation of a solid passive film on the ligaments of NP-Au during dealloying. Understanding the nature of such a passive film, and the conditions under which this film forms during electrolytic dealloying, is critical to determining its impact on both dealloying kinetics and the

properties/performance of as-synthesized NP-Au in energy applications. For example, a passive surface film created on NP-Au during dealloying may affect its porosity development mechanism by cutting off pathways for surface diffusion, thereby limiting ligament coarsening, and ultimately resulting in a smaller material.²⁷ When tested for its catalytic activity after dealloying, for example, the performance of this surface passivated NP-Au could yield different results compared to pure, non-passivated NP-Au. Considering that the formation of such a surface passive film directly depends on the nature of the electrolyte and the electrode used in an electrochemical process, to better serve the nanoporous metals community, we performed a broad literature search to identify the type of electrolytes widely used in the field to fabricate NP-Au from Au-Ag alloy. As shown in the table and corresponding pie chart in **Fig. 1**, we found that perchloric acid (HClO_4) and nitric acid (HNO_3) are the most used electrolytes for electrolytic dealloying. Interestingly, Weissmüller and co-workers carried out a comparative study on electrolytic dealloying of NP-Au in HClO_4 versus HNO_3 , and reported the following key findings (among others):¹⁶ (i) The complete removal of Ag from the Au-Ag parent alloy is slower in HClO_4 compared to HNO_3 ; (ii) The coarsening of the ligament/pore structures during dealloying is more severe in HNO_3 than in HClO_4 . In the present study, we hypothesized that the phenomena in (i)-(ii) are associated with the nature of the surface passive film formed with respect to the electrolyte. Thus, this article describes novel fundamental research aimed at identifying and understanding the conditions under which a surface passive film arises via side reactions during NP-Au formation by electrolytic dealloying in HClO_4 , the most used electrolyte for selective electrolytic leaching of Au-Ag alloys. While we do not study a specific energy application of NP-Au in this work, we aim to shed light on surface passive films, which could drastically impact the performance of NP-Au in its various energy applications.

(a)

Electrolyte	Molarity (M)	Reference Electrode	Applied Voltage vs. RE (mV)	Reference
AgNO ₃	0.1	NHE	1440-2000	15
	1	Ag	500	28
HClO ₄	1	Ag/AgCl	600-850	29
	1	Ag/AgCl	700	30
	1	Ag/AgCl	750	31
	1	Ag/AgCl	750	32
	1	Ag/AgCl	750	33
	1	Ag/AgCl	750	34
	1	Ag/AgCl	750-850	35
	1	Ag/AgCl	850	14
	1	Ag/AgCl	850	31
	1	Ag/AgCl	850	14
	0.7-0.8	Ag/AgCl	900-1000	36
	1	Ag/AgCl	1000	30
	1	Ag/AgCl	1050	16
	0.7	Ag/AgCl	0-1300	37
	1	Ag/AgCl	1050-1200	38
	0.77	MSE	920-1100	39
	0.5	MSE	550	40
	0.5	MSE	300	41
	1	SCE	1100	42
	1	SCE	1038	43
1	SCE	1070	44	
1	SCE	1040	45	
1	SCE	1100	46	
1	SCE	1000	47	
HNO ₃	5	Pt	60	2
	0.1	SCE	1100	48
	1	Ag	600	49
	5	Pt	60-300	50
	1	NHE	1175	51
	Dilute	Ag/AgCl	1300	52
	5	Pt	60	53
	5	Pt	60	16
5	Pt	60	54	

(b)

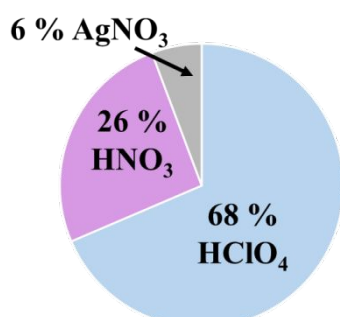


Fig. 1. (a) Survey of reports on NP-Au synthesized by electrolytic dealloying of Au-Ag parent alloys. Various electrolytes, molarities, reference electrodes, and applied anodic voltages are shown. Of the three electrolytes, HClO₄ is most widely used to synthesize NP-Au by electrolytic dealloying, followed by HNO₃. (b) Pie chart

indicating the percentage of reports found in our survey which use HNO_3 , HClO_4 , and AgNO_3 as the electrolytic dealloying electrolyte.

EXPERIMENTAL

In situ dealloying: We used a custom Kapton pouch cell containing three electrodes and 2 mL of electrolyte to dealloy the parent Au-Ag alloy. A 5 μm -thick Au-Ag parent alloy (Custom Order, Imtradex Corp.) with composition $\text{Au}_{35}\text{Ag}_{65}$ (at. %) was used as the working electrode, an Ag/AgCl in 1M KCl was used as the reference electrode, and Pt foil was used as the counter electrode. The masses of the parent alloys for HClO_4 dealloying and HNO_3 dealloying were 7.2 mg and 5.2 mg, respectively. The pouch cell was mounted to a sample stage in the environmental chamber at the Dual-Source and Environmental X-ray Scattering Facility at Penn and filled with either 1M HClO_4 or 1M HNO_3 , depending on the experiment. The environmental chamber was left at atmospheric pressure to avoid electrolyte evaporation. A BioLogic VMP-300 potentiostat was used to apply an oxidizing potential of 950 mV between the Au-Ag parent alloy and the Ag/AgCl reference electrode. The microstructural and crystallographic evolution was probed by aiming the Cu K_α beam at the Au-Ag parent alloy and detecting the scattered waves as Ag was oxidized. Microstructural data was gathered on a small-angle 1M Pixel Pilatus detector down an evacuated flight path, and crystallographic data was gathered on a 100K Pixel Pilatus wide-angle detector in the environmental chamber nearby the sample. Each acquisition was 180 seconds. After dealloying, the sample was washed in DI water several times to remove residual electrolyte and dried in air. We used 17 M liquid ammonia in water (Fisher, 28-30 % NH_4OH) to remove AgCl from the HClO_4 -dealloyed sample.

SAXS fitting: Each SAXS dataset was fit using the Teubner-Strey model, which captures the characteristic spacing d in bicontinuous materials.^{55,56}

Ex situ dealloying: Samples were dealloyed in the same electrolyte concentration (1 M HNO₃ and 1 M HClO₄) and at the same potential (950 mV) as the *in situ* experiments discussed above, this time with 10x volume of electrolyte (20 mL). The Hg/Hg₂SO₄ (in K₂SO₄, sat.) control experiment was performed in 2 mL of 1M HClO₄ at potential of 530 mV under nitrogen purge to suppress ORR (see **Eq. 4** under *Elucidation of the Reaction Mechanisms*).

Characterization: Scanning electron microscopy (SEM, JEOL 7500F) and energy dispersive X-ray spectroscopy (EDX, EDAX Octane Elect Super) were used to investigate the microstructure and elemental composition of the *in situ* dealloyed samples. *Ex situ* XRD patterns were collected using a Rigaku MiniFlex powder diffractometer with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed using PHI VersaProbe I instrument using a 200 μm 50 W beam for acquisition. A pass energy (PE) of 23 eV for high resolution spectra windows, and PE of 117 eV was used for the survey analysis. Dual source (electron and ion gun) charge compensation was used during analysis to compensate for the shifts in the BE of the spectra. The adventitious C 1s C-C peak at 285.0 eV was used to calibrate binding energy positions.

RESULTS AND DISCUSSION

1. Overview

As mentioned in the *Introduction*, during dealloying, the formation of a passive film at the electrode/electrolyte interface can impact the kinetics of the dealloying process and the morphology (e.g., structure size and crystallography) of the dealloyed material. The nature of this passive film directly depends on both the electrolyte and the electrode, and HClO₄ and HNO₃ are the most widely used electrolytes during electrolytic dealloying of Au-Ag parent alloys based on our broad literature survey in **Fig. 1**. In the case of HClO₄, we hypothesized that the Au-Ag parent alloy and the HClO₄ electrolyte may decompose and form insoluble compounds (e.g., silver chloride — AgCl), which may deposit on the surface of the NP-Au as

a passive film and hinder the dealloying rate. In the case of HNO_3 , the Au-Ag parent alloy and HNO_3 electrolyte may also decompose, but form products that are soluble in acid or form a non-blocking film (e.g., silver nitrate – AgNO_3 , or non-dense silver oxides – AgO_x species), which may not hinder the dealloying process in acids. To test our hypothesis, in the second part of the *Results and Discussion* section, we probe the evolution of the characteristic microstructural size (using SAXS) and crystallography (using WAXS) simultaneously during electrolytic dealloying in 1 M HClO_4 and 1 M HNO_3 . This is, to the best of our knowledge, the first time SAXS and WAXS have been used simultaneously to characterize the electrolytic dealloying of Au-Ag. In the third part of the *Results and Discussion* section, we use new insights gained from the SAXS and WAXS data to elucidate the electrochemical reaction mechanisms occurring during NP-Au formation by electrolytic dealloying in HClO_4 and HNO_3 , and the effects of the electrolyte on the dealloying process. In the fourth part of the *Results and Discussion* section we elucidate the mechanism through which AgCl forms. We also propose a mechanism for Ag and Au mobility (i.e., Ag atom dissolution and surface diffusion of Au atoms) during electrolytic dealloying in the presence of a passive AgCl , building on a recent model proposed by Snyder *et al.* on electrolytic dealloying in neutral pH in the presence of a passive silver oxide film.¹⁵ Finally, in the fifth and last part of the *Results and Discussion* section, we clarify how the presence of AgCl passive film can impact the performance of nanoporous gold in specific energy applications.

2. Small- and wide-angle X-ray scattering (SAXS and WAXS)

In situ SAXS and WAXS during electrolytic dealloying: SAXS and WAXS were used simultaneously and in real time to study the effects of HClO_4 and HNO_3 on the dealloying process. Combining these techniques, we investigated the temporal evolution of both the microstructure and the crystal structure of a 5 μm -thick Au-Ag parent alloy with composition $\text{Au}_{35}\text{Ag}_{65}$ at. % as Ag was removed from it electrolytically. The electrolytic dealloying setup

consists of an open-air Kapton pouch cell (see **Fig. S1** in the Electronic Supporting Information — ESI) containing the 5 μm -thick $\text{Au}_{35}\text{Ag}_{65}$ parent alloy used as the working electrode, a platinum (Pt) foil used as the counter electrode, a Ag/AgCl reference electrode, and 2 mL of either 1 M HClO_4 or 1 M HNO_3 used as the electrolyte (**Fig. S1**). This electrolytic cell was mounted in the chamber of a Xenocs Xeuss 2.0 scattering instrument as illustrated in **Fig. S2**, with the X-ray chamber at atmospheric pressure and ambient temperature in air. A constant voltage of 950 mV was applied between the Au-Ag working and Ag/AgCl reference electrodes to drive the dissolution of Ag. During electrolytic dealloying, X-rays generated using a copper K_α source (**Fig. S2a**) are monochromated and collimated (**Fig. S2b**), and impinge on the $\text{Au}_{35}\text{Ag}_{65}$ working electrode (**Fig. S2c**), interacting with it by transmission, absorption, or scattering. We found that the $\text{Au}_{35}\text{Ag}_{65}$ working electrode thickness used in our experiments (5 μm) balances these interactions to provide enough scattering intensity within our time resolution (180 seconds). The scattered waves are collected with two detectors: a small-angle detector at the end of an evacuated flight path for SAXS (**Fig. S2d**), and a wide-angle detector in the environmental chamber near the sample (**Fig. S2e**) for WAXS. In **Fig. S2f-g**, we explored two different electrolytic dealloying cell configurations: (i) A side-by-side configuration (**Fig. S2f**), where the working electrode (checkered film connected to the red line) and counter electrode (grey film connected to the blue line) sat side-by-side to avoid the interaction of the incident X-rays with the Pt foil electrode, which would otherwise weaken the intensity of the scattered X-rays collected in **Fig. S2d-e**. (ii) A stacked configuration (**Fig. S2g**), in which the working and counter electrodes face each other and are separated by a glass microfiber battery separator (Whatman, Grade GF/C) to prevent electrical shorting. Note that while this stacked configuration is ideal for electrochemical experiments because mass transport is optimal when the working and counter electrodes face each other, incident X-rays interacting with the Pt counter electrode weakens the intensity of the scattered X-rays collected in **Fig. S2d-e**. Therefore, after performing *ex situ* experiments to ensure that electrolytic dealloying proceeds

similarly in the two cell configurations in **Fig. S2f-g** (see **Supporting Video 1** and **Fig. S3** for *ex situ* dealloying using the stacked configuration in **Fig. S2g**), we use the side-by-side configuration (**Fig. S2f**) for subsequent experiments. A detailed diagram of this setup is found in **Fig. S1**.

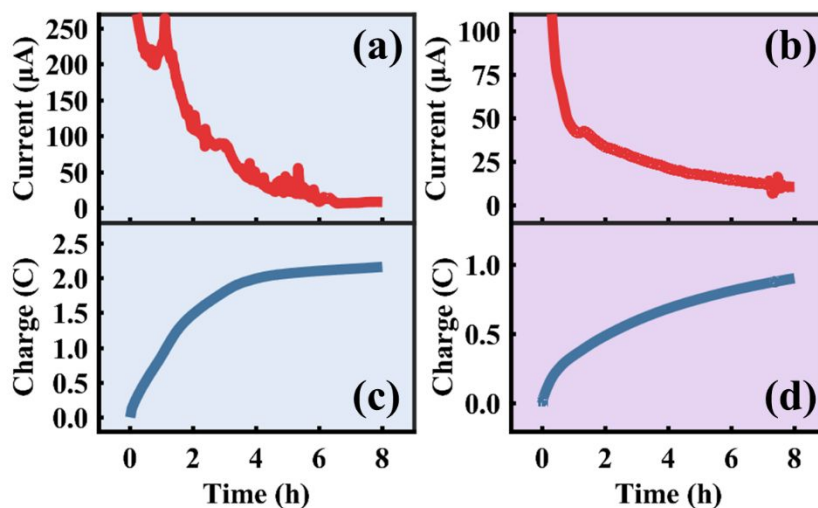


Fig. 2. Current and charge transferred during the first eight hours of the *in situ* sample dealloyed in HClO₄ (a & c) and HNO₃ (b & d).

The *in situ* electrolytic dealloying data obtained are shown in **Fig. 2** with background colors corresponding to the electrolyte: blue for HClO₄, and purple for HNO₃ (similar background colors are also used in **Figs. 3-6**, and **Figs. S3-8**). The current vs. time plots in **Fig. 2a-b** represent the typical electrolytic dealloying currents measured between the Au₃₅Ag₆₅ working electrode and the Pt counter electrode when a constant voltage of 950 mV is applied between the working and the Ag/AgCl reference electrode in 1 M HClO₄ electrolyte (**Fig. 2a**) and 1 M HNO₃ electrolyte (**Fig. 2b**). In **Fig. 2a**, there is a fluctuation in current around the end of the first hour of dealloying, which has been known to occur during electrolytic dealloying experiments when the dissolution of the sacrificial element (in our case Ag) does not occur uniformly. Typically, during dealloying, if the Ag dissolution front at the bulk electrode/electrolyte interface propagates uniformly (i.e., layer-by-layer) inside the material, the dealloying current measured across the cell (i.e., the Ag dissolution current) will be constant without fluctuation. In practice, however, Ag dissolution does not occur layer-by-layer: in

addition to Ag removed from the bulk electrode/electrolyte interface, the electrolyte can also penetrate into the bulk of the material through cracks and grain boundaries to remove more Ag. This will cause the dealloying current to suddenly increase/fluctuate as shown **Fig. 2a**. Similar fluctuations have been observed in our previous work on electrolytic dealloying.⁵⁷ The corresponding plots of the cumulative charge as a function of time associated with the amount of Ag removed during the dealloying process are shown in **Fig. 2c-d** for HClO₄ and HNO₃, respectively. Note that in our pouch cell configuration, the AuAg parent alloy is partially submerged into solution, and a portion of the AuAg alloy remains outside of the electrolyte to connect with the lead wire (see **Fig. S2**). The magnitude of current in **Fig. 2a** and **Fig. 2b** is therefore associated with the active mass. We should emphasize that a difference in current magnitude does not impact our SAXS and WAXS results below as the same oxidizing potential was used (950 mV vs. Ag/AgCl) and porosity development was observed in both cases.

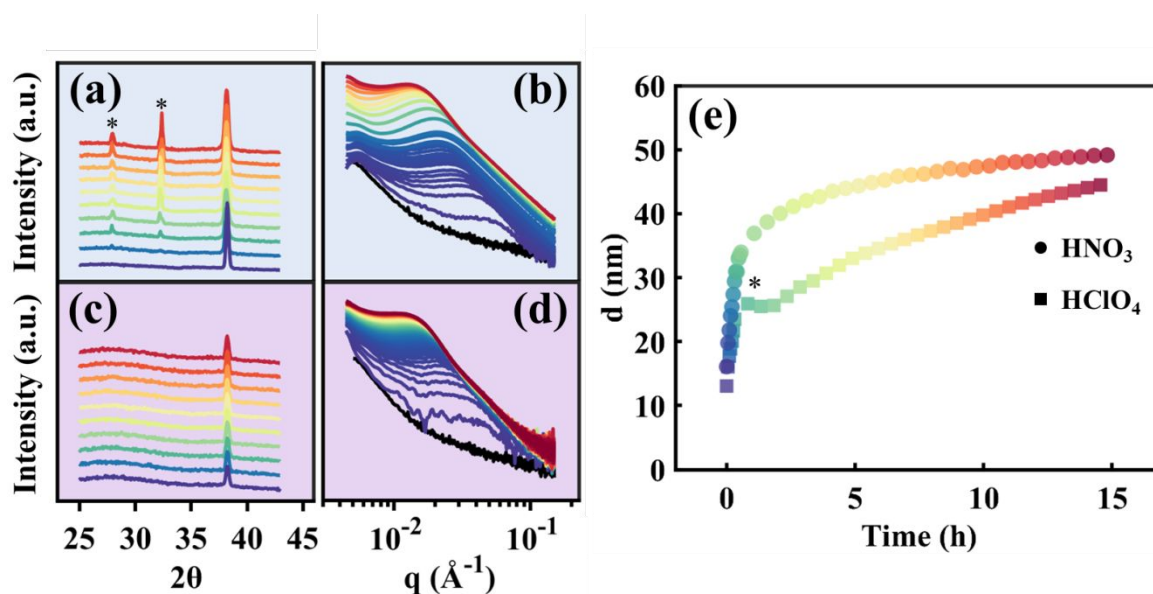


Fig. 3. Real-time data. Comparative view of SAXS and WAXS data during the electrolytic dealloying of a parent Au-Ag alloy into NP-Au using HClO₄ (a & b), and HNO₃ (c & d). In the WAXS data for the *in situ* HClO₄ cell (a), two peaks appear which correspond to AgCl, represented by asterisks. No such peaks arise during electrolytic dealloying in HNO₃ (c). (e) The ligament-ligament distance d of the NP-Au growing in each of the two electrolytes. HNO₃ grows rapidly at first and eventually reaches a regime of slow growth/stability, where HClO₄ grows at a similar pace at first, but is slowed after reaching ~25 nm.

Time-resolved SAXS and WAXS collected *in situ* during Ag removal from the Au₃₅Ag₆₅ parent alloy are shown in **Fig. 3a-b** for HClO₄ and **Fig. 3c-d** for HNO₃. Time in these datasets is indicated by color, beginning in purple and ending in red. The black curve in **Fig. 3b-d** is the pattern of the starting Au₃₅Ag₆₅ parent alloy. **Fig. 3e** shows the average ligament-ligament distance, d , for the sample dealloyed in HClO₄ (squares) and in HNO₃ (circles) deduced from the SAXS data from **Fig. 3b-d**.^{55,56} Note that in **Fig. 3e**, the bump marked by an asterisk for the sample dealloyed in HClO₄ is an experimental artifact as it has not been observed in other d versus time curves as shown in **Fig. S4** in the ESI.

Evolution of the crystal structure from WAXS data: To elucidate the effect of the two electrolytes on the electrolytic dealloying process, we begin by noting the striking difference between the WAXS patterns for the samples dealloyed in HClO₄ (**Fig. 3a**) and HNO₃ (**Fig. 3c**). On the one hand, the WAXS patterns for electrolytic dealloying in HNO₃ (**Fig. 3c**) show the (111) peak associated with the face-centered cubic (FCC) crystal structure of the starting Au₃₅Ag₆₅ evolving to NP-Au. No new peaks were observed during dealloying. A video showing the evolution of this peak in real time is provided in the ESI as (**Supporting Video 2**). On the other hand, the WAXS patterns for electrolytic dealloying in HClO₄ (**Fig. 3a**) also shows the (111) peak for the Au-Ag solid solution evolving to NP-Au, but during the process two new peaks appear at the 2θ values of 27.8 and 32.3, respectively, as indicated by the asterisks in **Fig. 3a**. These peaks are attributed to AgCl (111) and (200). A close look at the time-evolution of these AgCl peaks reveals that they are not present at the beginning of the dealloying process. Instead, they appear after 1 h and gradually increase in intensity during electrolytic dealloying. A video showing the evolution of these peaks in real time can be found in the ESI (**Supporting Video 3**).

Ex situ X-ray diffraction (XRD) after electrolytic dealloying: To confirm that AgCl formed on NP-Au during dealloying, the NP-Au dealloyed in the X-ray scattering instrument was rinsed in deionized (DI) water (note that AgCl is insoluble in DI water) and further characterized *ex situ* by XRD. The presence of AgCl was confirmed as shown by the blue pattern in **Fig. 4a**, where it is seen that the diffraction peaks of AgCl marked by the asterisks match with the black triangle pattern associated with AgCl (PDF # 31-1238). Furthermore, the relatively strong AgCl peak intensity indicates that it is a non-negligible component in the system. On the other hand, the *ex situ* XRD of the sample dealloyed in HNO₃ contains peaks solely from Au (PDF # 4-784) as shown by the blue curve in **Fig. 4b**.

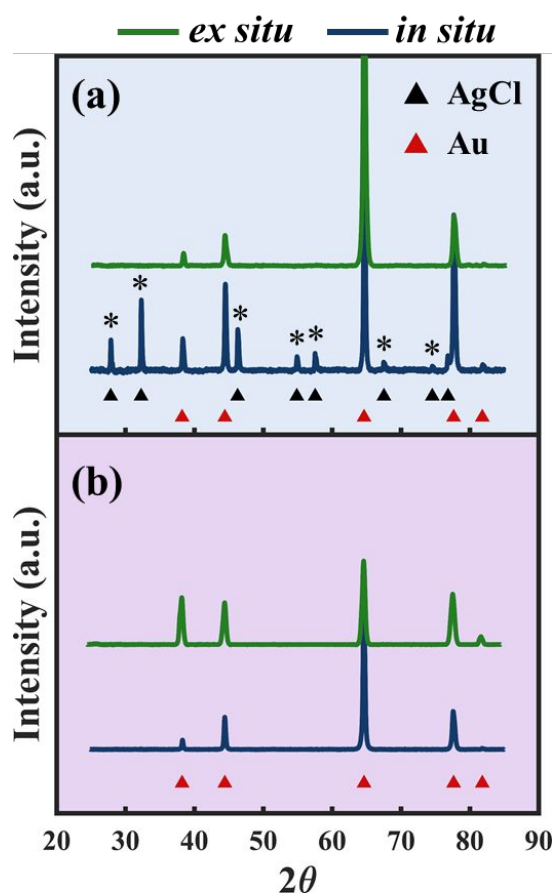


Fig. 4. (a) XRD patterns after dealloying in 1M HClO₄ in small volumes (*in situ*, blue) and in large volumes (*ex situ*, green). Asterisks mark the AgCl peaks (PDF 31-1238) formed during *in situ* dealloying. (b) XRD patterns after dealloying in 1M HNO₃ in small volumes (*in situ*, blue) and in large volumes (*ex situ*, green).

Structure size evolution from SAXS data: While not immediately noticeable from the SAXS patterns in **Fig. 3b-d**, the microstructure of each of these systems evolves differently in time as indicated by the variation of d with time shown in **Fig. 3e**. To reiterate, d is the characteristic wavelength in the system, a variable closely related to the peak position in inverse space (q) observed in the scattering patterns in **Fig. 3b-d**, and is roughly double the ligament size. We have employed the Gaussian Random Field (GRF)^{56,58,59} model to provide representative real-space nanoporous structures at different stages of the dealloying process (**Fig. S5** in the ESI). Here, we extract real values of d from the dealloying process in HClO₄ and HNO₃ from **Fig. 3e** and plug them into the GRF model to visualize how the microstructure changes as a function of dealloying time in each case. When dealloying in HNO₃, d increases rapidly from an initial value of 16 nm (corresponding to an average ligament size of ~8 nm) to 40 nm (corresponding to a ligament size of ~20 nm) within the first 2 h (circles in **Fig. 3e**), and eventually reaches a slower growth regime. When dealloying in HClO₄, d increases from a value of ~13 nm (corresponding to a ligament size of ~6.5 nm) to ~26 nm (corresponding to a ligament size of ~13 nm) within the first 2 h. The change in d for dealloying in HClO₄ ($\Delta d = 13$ nm) within these first two hours is nearly half that of the change in d observed for dealloying in HNO₃ ($\Delta d = 24$). These observations clearly suggest that the initial growth and coarsening of the ligament and pore structures in NP-Au during dealloying is more severe in HNO₃ than in HClO₄, and as a result the feature size of NP-Au is larger for the sample dealloyed in HNO₃ than the one dealloyed in HClO₄. These findings are in agreement with previous report by Weissmüller and co-workers, a comparative study on electrolytic dealloying of NP-Au in HClO₄ versus HNO₃.¹⁶ Towards the end of the experiment, the structure size (d) of the HClO₄-dealloyed sample nearly intersects with that of the HNO₃ sample, indicating that the coarsening process occurs over longer periods of time in HClO₄ compared to HNO₃. Thus, given enough time, the structural size of NP-Au dealloyed in HClO₄ becomes similar to NP-Au dealloyed in HNO₃ as will be shown by electron microscopy in the following section.

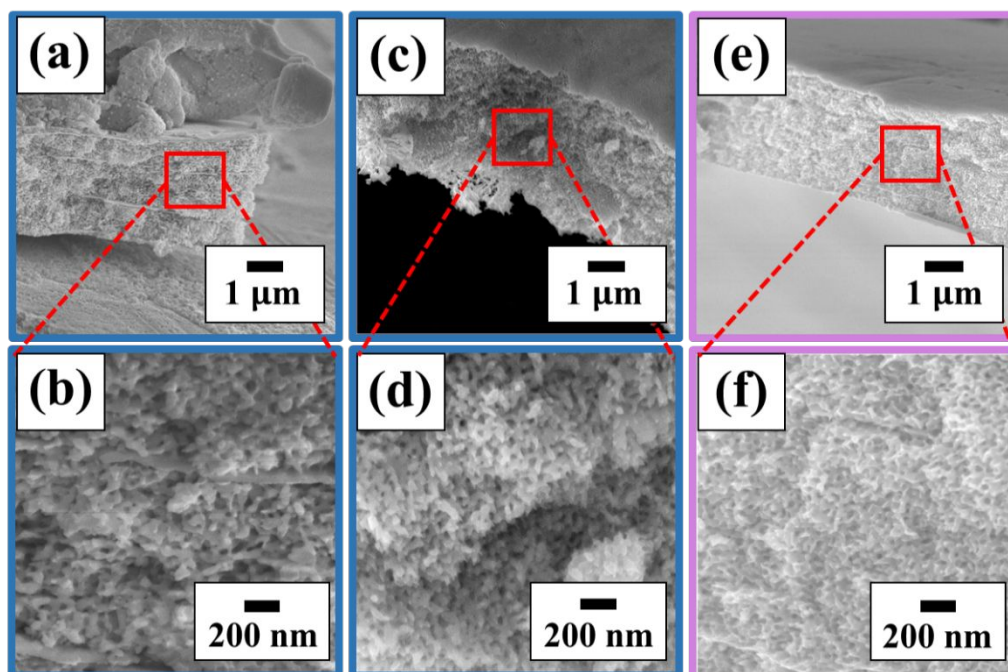


Fig. 5. SEM images of *in situ* dealloyed NP-Au. (a & b) NP-Au dealloyed in HClO_4 , with large AgCl particles on the top surface of the film. (c & d) NP-Au dealloyed in HClO_4 and washed in 17 M NH_3 to remove residual AgCl particles. (e & f) NP-Au dealloyed in HNO_3 .

Characterization by electron microscopy and x-ray photoelectron spectroscopy: Scanning electron microscopy (SEM) was used to further investigate the morphology of each of the two samples dealloyed in HClO_4 and HNO_3 in real time during X-ray scattering (i.e., from **Fig. 2** & **Fig. 3**). Typical SEM images of the cross sections are shown at low and high magnifications in **Fig. 5**. For the HClO_4 -dealloyed sample (**Fig. 5a-b**), we noticed a thick and dense film on top of dealloyed NP-Au at a low magnification (**Fig. 5a**). The expected NP-Au morphology can be observed at a high magnification (**Fig. 5b**). Further analysis by energy-dispersive X-ray spectroscopy (EDX) elemental mapping (see **Fig. S6**) indicates that the bulk of NP-Au mostly contains Au with small amounts of Ag and Cl, while the thick film on top of NP-Au only contains Ag and Cl. This is in good agreement with the presence of AgCl detected from the WAXS and XRD data of the HClO_4 -dealloyed sample. Considering the insolubility of AgCl in water, the HClO_4 -dealloyed sample was washed in concentrated liquid ammonia (17 M NH_3)

which is known to dissolve silver halides.⁶⁰ The thick AgCl is removed when the sample is washed in 17 M NH₃, as shown in **Fig. 5e-f**, and further **Fig. S6** in the ESI. In contrast to the HClO₄-dealloyed sample (**Fig. 5a-b**), the sample dealloyed in HNO₃ does not have any surface film as shown in **Fig. 5c-d**. It should be emphasized that the presence of a small amount of Ag and Cl in the bulk of NP-Au dealloyed in HClO₄ as mentioned above suggests that the AgCl film may also be present on the ligaments of NP-Au as will be confirmed later using (XPS). The presence of such a passive AgCl film on the ligaments of NP-Au will impact the kinetics of the dealloying process and the growth and coarsening of these ligaments, which may explain our earlier observation (from the SAXS data) that during dealloying, the ligaments and pores are larger for the NP-Au dealloyed in HNO₃ than the one dealloyed in HClO₄. This aspect will be discussed at length in a later section of this work. For now, since both WAXS, XRD, SEM, and EDX mapping confirm the presence of a thick AgCl film on the NP-Au dealloyed in HClO₄, the straightforward question that arises is why such film has not been detected and reported earlier considering that 1 M HClO₄ is the most used electrolyte for electrolytic dealloying as shown in **Fig. 1**. To answer this question, we must stress that a relatively large volume (several tens of mL) of 1 M HClO₄ is commonly used during electrolytic dealloying, whereas only ~2 mL of 1 M HClO₄ was used in our electrolytic cell during *in situ* dealloying in the X-ray scattering instrument. In such a small volume, the sacrificial Ag which is removed from the Au-Ag parent alloy would impart a significantly higher Ag⁺ ion concentration to the electrolyte compared to larger volumes. This would lead to an increase in AgCl precipitation. To verify this hypothesis, we carried out *ex situ* dealloying for both HClO₄ and HNO₃, this time in 20 mL of electrolyte (a 10-fold increase in electrolyte volume), and used both XRD (**Fig. 4**) and XPS (**Fig. 6**) to characterize these films after dealloying. The sole peaks in the *ex situ* XRD patterns for the samples dealloyed in HClO₄ (green line in **Fig. 4a**) and HNO₃ (green line in **Fig. 4b**) are for Au. If a very thin film of AgCl was present on the NP-Au (unlike the dense film observed from our *in situ* tests in small electrolytes), it may not be detected by XRD, a bulk technique

which does not have significant surface sensitivity. We believe this is the reason that, although HClO_4 is the most widely used electrolyte for electrolytic dealloying, the presence of AgCl on the dealloyed NP-Au has not been reported prior to the present work.

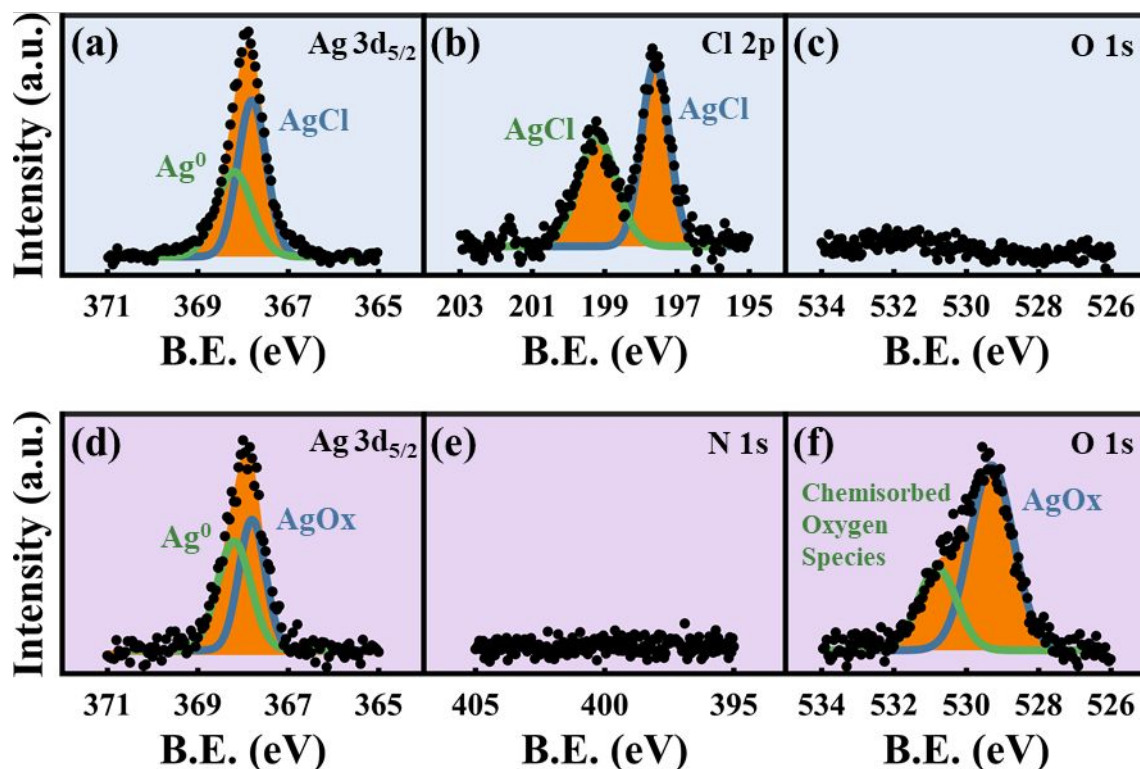


Fig. 6. XPS Spectra. Top row is for the HClO_4 -dealloyed *ex situ* sample: (a) $\text{Ag } 3d_{5/2}$, (b) $\text{Cl } 2p$ and (c) $\text{O } 1s$, demonstrating AgCl growth even in larger electrolyte volumes. Bottom row is for the HNO_3 -dealloyed *ex situ* sample: (d) $\text{Ag } 3d_{5/2}$, (e) $\text{N } 1s$ and (f) $\text{O } 1s$, demonstrating that there is no nitrogen-containing surface coating.

While previous reports have used XPS to analyze the surface states of dealloyed NP-Au, these studies focus mostly on elemental Ag, Au, and O,^{38,61,62} and not on the electrolyte species. XPS surveys of the surface of the HClO_4 - and HNO_3 -dealloyed NP-Au samples are provided in **Fig. S7** in the ESI. The corresponding high-resolution scans associated with $\text{Ag } 3d_{5/2}$, $\text{Cl } 2p$, and $\text{O } 1s$ are shown in **Fig. 6a-c** for the HClO_4 -dealloyed NP-Au. Similarly, the high-resolution scans associated with $\text{Ag } 3d_{5/2}$, $\text{N } 1s$, and $\text{O } 1s$ are shown in **Fig. 6d-f** for the HNO_3 -dealloyed NP-Au. Starting with the high resolution $\text{Ag } 3d_{5/2}$ spectra, the deconvoluted peaks for the HClO_4 -dealloyed NP-Au in **Fig. 6a** indicate the presence of metallic silver (Ag^0) and AgCl as illustrated

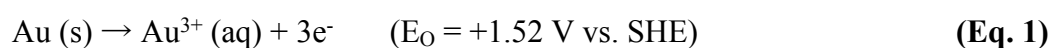
by the Ag 3d_{5/2} peaks at 368.2 eV (green curve) and 367.8 eV (blue curve) associated with the binding energies of Ag⁰ and Ag⁺, respectively.⁶³ The deconvoluted peaks for the HNO₃-dealloyed NP-Au in **Fig. 6d** also indicate the presence of Ag⁰ and oxidized silver species (AgO_x) as illustrated by the Ag 3d_{5/2} peaks at 368.2 eV (green curve) and 367.8 eV (blue curve) associated with the binding energies of Ag⁰ and Ag⁺, respectively.⁶³ This AgO_x can form during dealloying (including residual Ag₂O, which is known to dissolve in acids). Next, to further support the presence of AgCl and AgO_x, we analyzed the high-resolution scans associated with electrolyte elements, namely Cl 2p and O 1s for the HClO₄-dealloyed NP-Au, and N 1s and O 1s for the HNO₃-dealloyed NP-Au. For the HClO₄-dealloyed NP-Au, **Fig. 6b** shows two peaks in the Cl 2p scan around 197.6 eV and 199.2 eV, which match well with the binding energies of Cl 2p_{3/2} and Cl 2p_{1/2},^{64,65} and can be attributed to AgCl. Further, the lack of a peak in the O 1s spectrum in **Fig. 6c** rules out any possibility that there is unwashed HClO₄ electrolyte on the sample. Thus, it can safely be concluded that even though AgCl could not be detected by XRD on NP-Au samples dealloyed *ex situ* using a relatively large volume of HClO₄ (green line, **Fig. 4a**), XPS data clearly suggest that AgCl is present on the surface of these NP-Au samples. For the HNO₃-dealloyed NP-Au sample, there is no peak in N 1s region in **Fig. 6e**, which is expected as nitrogen-containing species such as AgNO₃ are very soluble in acids. However, there is an oxygen signal (O 1s spectrum) in **Fig. 6f**, which can be deconvoluted into a broad peak around 529.3 eV (blue curve) ascribed to AgO_x, and a smaller peak at 530.8 eV (green curve), which is ascribed to chemisorbed oxygen.⁶³ Because AgCl is insoluble in most acids, the AgCl film formed during dealloying in HClO₄ remains on the surface of NP-Au during dealloying. This will hinder the rate of sacrificial Ag dissolution and surface diffusion of Au atoms and thus slow down the kinetics of the dealloying process and the rate of ligament growth/coarsening. Indeed, Snyder *et al.* reported that passive silver oxide films can form during electrolytic dealloying in a neutral pH (AgNO₃) electrolyte, and proposed a mechanism for the hindrance Au and Ag mobility in their system.¹⁵ We will return to this mechanism later

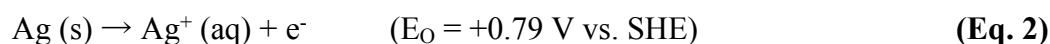
in this article, and build on its insight for the present results on HClO₄. In contrast to HClO₄, since AgO_x compounds formed during dealloying in HNO₃ are soluble in acids, the rate of sacrificial Ag dissolution and surface diffusion of Au atoms during dealloying is less hindered, and thus kinetics of the dealloying process and rate of ligament growth/coarsening is not hampered. The O 1s signal in **Fig. 6f** indicates that some of the AgO_x formed has been trapped on the pore walls during the dealloying. In order to form the passive AgCl film, there must be a source of Cl⁻ ions to react with the Ag⁺ ions oxidized at the Au-Ag working electrode. The possibility of Cl⁻ originating from the Ag/AgCl reference electrode was ruled out by performing control experiments using mercury/mercurous sulfate (Hg/Hg₂SO₄) as a reference electrode which does not contain Cl⁻. In other words, in our control experiments the only source of Cl⁻ ions is the HClO₄ electrolyte. Interestingly, XRD still shows that AgCl is present on the NP-Au after dealloying as shown in **Fig. S8** in the ESI.

3. Elucidation of the reaction mechanisms

In this section, we elucidate the reaction mechanisms through which Cl⁻ and AgCl form during electrolytic dealloying in HClO₄, as well as the reaction mechanisms associated with free corrosion and electrolytic dealloying in HNO₃.

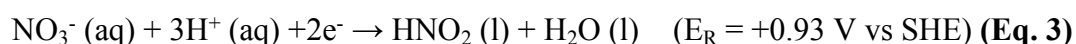
Main reactions: In general, two half-reactions take place during both free corrosion and electrolytic dealloying: (i) an oxidation half-reaction during which the sacrificial element (here Ag) is dissolved; and (ii) a reduction half-reaction during which ionic or gaseous species in the electrolyte are reduced. Starting with the oxidation half-reaction associated the free corrosion or electrolytic dealloying of a Au-Ag parent alloy, both Au and Ag are susceptible to dissolve through **Eq. 1** and **Eq. 2**, respectively, depending on strength of the corroding medium for free corrosion dealloying, and the magnitude of the applied potential for electrolytic dealloying.⁶⁶



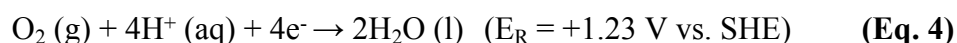


Typically, in order to oxidize Ag and leave Au behind un-oxidized to create NP-Au by electrolytic dealloying, the magnitude of the voltage applied must be greater than 0.79 V vs. SHE but less than 1.52 V vs. SHE. In all of the electrolytic dealloying experiments in HClO₄ and HNO₃ done in the present work, the applied voltage sat between these potentials at 0.95 V vs. Ag/AgCl, which corresponds to 1.17 V vs. SHE.⁶⁶

Next, we discuss the reduction half-reaction associated with free corrosion and electrolytic dealloying. In free corrosion dealloying (i.e. etching away Ag in concentrated HNO₃ without using an external bias), the counter reaction to **Eq. 2** is the reduction of nitrate ions, which occurs spontaneously through **Eq. 3** and provides sufficient potential to oxidize Ag:^{66,67}



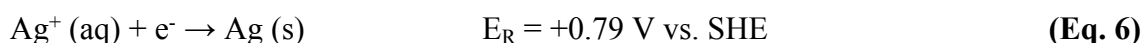
In practice, for free corrosion dealloying to occur, highly concentrated HNO₃ is necessary to overcome the high reaction overpotentials by increasing the potential of the reduction half-reaction in **Eq. 3**.⁶⁷ For example, the potential of **Eq. 3** is increased from 0.93 V to 1.07 V vs. SHE if the concentration of HNO₃ is increased from 1 M to 15 M. In other words, for the present work, Ag removal from Au-Ag by free corrosion in 1 M HNO₃ through **Eq. 2** in combination with **Eq. 3** is not kinetically favorable. Instead, a bias voltage is used to electrolytically dissolve Ag through **Eq. 2** in combination with an appropriate reduction half-reaction. This reduction reaction takes place at the Pt counter electrode during electrolytic dealloying. To our knowledge, the nature of the counter half-reaction has not been reported and needs to be identified. For electrolytic dealloying in HClO₄ we identify three candidates for reduction at the Pt counter electrode. The first is O₂, which in acidic solution can be reduced in the oxygen reduction reaction (ORR) in **Eq. 4**:



The second is ClO₄⁻, which can decompose into Cl⁻ ions through **Eq. 5**.⁶⁸

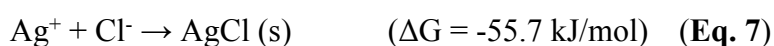


And finally, Ag plating is possible based on **Eq. 6**:



Thermodynamically, when there are many possible reduction half-reactions, the one with the highest reduction potential proceeds first (i.e., the ClO_4^- reduction reaction in **Eq. 5**). However, if the reaction kinetics are sluggish, a reduction half-reaction with lower reduction potentials may proceed first. Out of the three possible counter reactions in **Eq. 4-6**, the kinetics of the Ag^+ deposition onto the counter electrode through **Eq. 6** is expected to be very favorable, but this reaction cannot occur before Ag^+ ions are sufficiently present in solution. Thus, the only possible reactions in the early stages of dealloying are ORR (**Eq. 4**) and ClO_4^- reduction (**Eq. 5**). In practice, **Eq. 4** and **Eq. 5** are kinetically sluggish but Pt catalyzes both of these reactions and thereby reduces their overpotentials.^{68,69} It is well-known in the electrocatalysis community that for the ORR reaction in **Eq. 4** to proceed continuously, the electrolyte should be saturated with O_2 gas, which is not the case during our electrolytic dealloying process. Therefore, we point to the reaction in **Eq. 5** as the main counter half-reaction during electrolytic dealloying in HClO_4 in combination with **Eq. 2**. At a later stage of the dealloying process (when the concentration of Ag^+ in the electrolyte is high enough), the half-reaction in **Eq. 6** may proceed. This can be confirmed by the presence of metallic Ag on the Pt counter electrode.

Side reactions: During electrolytic dealloying in HClO_4 , Cl^- are created at the counter electrode through the reduction of ClO_4^- in **Eq. 5** spontaneously reacts ($\Delta G < 0$) with Ag^+ produced at the working electrode through the oxidation half-reaction in **Eq. 2** to form $\text{AgCl} (\text{s})$ through **Eq. 7**:



This $\text{AgCl} (\text{s})$ product is insoluble in water,⁶⁰ and thus remains on NP-Au. On the other hand, the counter reactions in HNO_3 do not form products that can react with Ag^+ to form a blocking film on the surface. In addition to ORR (**Eq. 4**) and Ag plating (**Eq. 6**), NO_3^- can be reduced to

HNO_2 (l) in **Eq. 3**, and gaseous products including NO_2 (g) and NO (g).⁶⁶ Ag^+ ions neither react with the electrolyte ions (NO_3^-), nor the reaction products in **Eq. 3**, to form an insoluble blocking film, as evidenced by a lack of N species in our XPS data in **Fig. 6e**.

4. Proposed mechanism of Au and Ag mobility in the presence of a passivating AgCl film

Based on the early understanding of the porosity evolution mechanism during dealloying,¹³ during selective leaching of a Au-Ag parent alloy, sacrificial Ag atoms dissolve in the electrolyte while Au atoms remaining at the electrode/electrolyte interface diffuse about to form Au clusters, which further grow into coarsened ligaments (i.e. post-dealloying coarsening). This mechanism, however, assumes a “clean” electrode/electrolyte interface that only comes into contact with the electrolyte and does not contain a passivating surface film. The presence of a passivating AgCl surface film at the electrode/electrolyte interface as reported in our work will hinder the mobility of Ag and Au atoms. The first model of the porosity evolution mechanism during dealloying that takes into account a passivating film was reported by Snyder *et al.*¹⁵ Their study involved creating nanoporous Au by electrolytic removal of Ag from a Au-Ag parent alloy in a neutral pH electrolyte, an aqueous solution of AgNO_3 , to circumvent using corrosives such as HNO_3 or HClO_4 . In their work, they reported the formation of a silver oxide (Ag_xO) passivating film during electrolytic dealloying, which hinders Ag and Au mobility and slows down the ligament coarsening significantly. The authors proposed a mechanism for Au surface diffusion and Ag dissolution in the presence of a Ag_xO passive film based on local pH gradients. They suggested the existence of the following three regions inside the pores.¹⁵

Region 1: The etch front, which has a lower pH compared to the rest of the pore. This region of low pH facilitates the dissolution of Ag and surface diffusion of Au. *Region 2:* The intermediate region adjacent to the etch front, where the Ag_xO layer starts to form. *Region 3:* The porous channels through which removed Ag^+ ions diffuse and dissolve into the bulk electrolyte. Based on our results from SAXS, WAXS, SEM, EDX, XRD, and XPS, we build on the above model of Snyder *et al.*, to explain the hindrance of Ag and Au mobility in our

system, and propose the following regions within a nanopore which we graphically depict in **Fig. 7** adapted from the work of Snyder *et al*¹⁵:

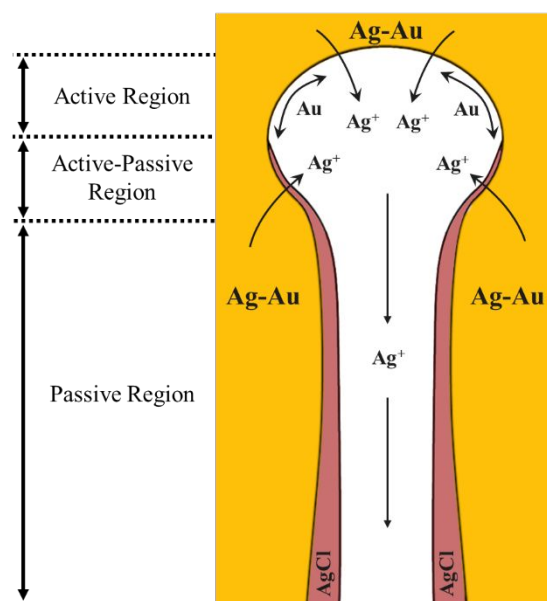


Fig. 7. Au and Ag mobility mechanism in the presence of a passivating AgCl film formed during dealloying in HClO₄. The three regions proposed are as follows: (1) Active region: the etch front without a passive film, where Ag atoms can oxidize from the bulk Ag-Au electrode and Au is free to diffuse on the pore wall. (2) Active-passive region of competing dissolution of Ag and AgCl formation. (3) Passive region: A region where Ag oxidation from the bulk Au-Ag electrode is not possible due to a thick, passive AgCl film in the pore channel. Illustration adapted from the work of Snyder *et al.*¹⁵

Active region: Since dealloying occurs in our system, this necessitates an etch front that facilitates Ag atom dissolution and surface diffusion of Au. This corresponds to *Region 1* from the work of Snyder *et al.* We call this region the *active region* as in the field of corrosion science.⁷⁰ In this region, the mobility of Ag and Au is not hindered.

Active-Passive region: Since a passivating AgCl film forms, there has to be a region adjacent to the etch front where this AgCl film nucleates. This corresponds to *Region 2* from the work of Snyder *et al.* More importantly, since the formation of a fully blocking AgCl film is a gradual process (i.e., it does not suddenly block Ag atom diffusion out of the bulk Au-Ag alloy), we speculate that in this second region, the formation of AgCl formation occurs concurrently with the corrosion of sacrificial Ag. This means that some Ag can still diffuse through the AgCl film

to go into the pore channel and dissolve into the electrolyte. Thus, in this second region, there is a competition between Ag dissolution and AgCl formation similar to common passivation processes in the field of corrosion science. We call this region the *active-passive region*.⁷⁰ In this region, the mobility of Ag and Au is partially hindered by a relatively thin AgCl film.

Passive region: As the AgCl film grows thicker, Ag diffusion through it will become more and more difficult, to the point where the AgCl will block its diffusion into the pore channel and dissolution into the electrolyte. Thus, a fully blocking AgCl film forms. This corresponds to *Region 3* from the work of Snyder *et al.* We call this region the *passive region*.⁷⁰ In this region, the mobility of Ag and Au is totally hindered by a blocking AgCl film.

5. Impact of passive film on energy applications.

Various energy applications based on NP-Au can be impacted by this AgCl passive film. Two of them include the use of NP-Au as an (electro)catalyst,^{2,71} and as an electrochemical actuator to convert electrochemical energy into mechanical energy.⁷²⁻⁷⁷ In the former case, the remarkable (electro)catalytic performance of NP-Au made by selective removal of Ag from Au-Ag alloys is usually attributed to specific catalytic sites such as {100} facets, or to residual sacrificial Ag atoms near the surface of NP-Au.^{2,71} The presence of a passive film at the surface of NP-Au will obviously prevent these active catalytic sites from coming in direct contact with the liquid or gas reactant, in order for the catalytic reaction to take place. This raises a fundamental question pertaining to the origin of the remarkable (electro)catalytic performance of dealloyed nanoporous metals. In the latter case, nanoporous metals have been reported to perform very well as electrochemical actuators,⁷²⁻⁷⁷ known as metallic muscles,⁷⁸ in which the actuation mechanism takes advantage of charge-induced changes in surface stress.^{72,79,80} An unexpected sign-inversion in the surface stress response of nanoporous metals has recently been reported during electrochemical actuation.^{14,74} Such a sign-inversion response was associated

with a passive film present at the internal surface of freshly dealloyed nanoporous metals.^{14,74} Hence, passive films directly impact the performance of nanoporous metal electrochemical actuators.

Conclusion

In summary, X-ray scattering techniques (SAXS and WAXS) were used in real time during NP-Au formation by selective electrolytic removal of Ag from a Au-Ag parent alloy (dealloying) in 1 M HClO₄ and 1 M HNO₃ electrolytes. We studied the impacts of side reactions on the reaction kinetics and on the morphology of the fabricated NP-Au in each of these electrolytes. By combining *in situ* SAXS and WAXS data with *ex situ* XRD, SEM, EDX, and XPS data, it was found that during electrolytic dealloying in HClO₄, the Ag⁺ ions released during Ag oxidation at the Au-Ag working electrode spontaneously react with Cl⁻ ions released during the reduction of ClO₄⁻ ions on the Pt counter electrode to form an insoluble AgCl passive film on the surface of NP-Au. We propose a mechanism for Au and Ag mobility in the presence of a passivating AgCl film formed during electrolytic dealloying in HClO₄, building on insights from a previous report of passive film formation during electrolytic dealloying in neutral pH. The presence of the AgCl film at the Au-Ag/HClO₄ interface is expected to hinder both the dissolution of Ag into the electrolyte and the surface diffusion of Au atoms left behind, which will ultimately slow down the dealloying reaction kinetics and the rate of ligaments growth and coarsening. During electrolytic dealloying in HNO₃, on the other hand, it was found that AgO_x forms at the Au-Ag/HNO₃ interface. However, because AgO_x compounds are very soluble in acids, they do not form an ion-blocking passive film at the electrode/electrolyte interface even though residual AgO_x can be trapped in the pores of NP-Au during dealloying. As a result, the reaction kinetics are less hampered in HNO₃ and the ligaments grow larger during the initial stages of dealloying. These new insights should contribute to a better understanding of the

reaction mechanisms in dealloying, and to a better control of the morphology and surface chemical state of dealloyed nanoporous metals for specific applications.

Electronic supplementary information

Electronic supplementary information (ESI) is available. See DOI:10.xxxxxxxx

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