Individual Hg microdroplet electrodes were used to perform Ge electrochemical liquid-liquid-solid (ec-LLS) crystal growth in aqueous solutions containing dissolved GeO2. The Hg microdroplets were prepared by electrodeposition of Hg onto pre-existing Pt ultramicroelectrodes ($r < 10 \mu m$). These Hg microdroplet ultramicroelectrode platforms were then used for analyses of Ge ec-LLS by both voltammetry and amperometry. Voltammetric responses indicated that Ge was neither immediately nor quantitatively dissolved into Hg upon electroreduction of aqueous solutions of GeO2. Separately, chronocoulometry performed at large overpotentials for reduction of dissolved GeO2 yielded crystalline Ge but with notable differences as compared to ec-LLS at a bulk Hg pool electrode. One set of experiments featured the surface of the Hg microdroplets possessing a complete Ge shell. The data suggested this shell formed within the first 1000 s and essentially passivated the electrode against further heterogeneous GeO2 reduction but allowed limited H+ reduction. The other set of experiments exhibited a similar shell but with fissures or cracks that exposed fresh Hg to the electrolyte and allowed Ge electrodeposition to persist much longer. In these experiments, hollow, spiral crystalline Ge tubes were extruded from the interior of the Hg microdroplets.

To date, a variety of bottom-up methods including vapor-liquid-solid growth,1-5 solution-liquid-solid growth,6,7 and template-defined electrodeposition8,9 have been demonstrated for the preparation of crystalline semiconductor micro/nanomaterials.8,9 A newly identified method is electrochemical liquid-liquid-solid (ec-LLS) crystal growth, where a liquid metal electrode acts both as the source of electrons for heterogeneous reduction reactions and as the solvent for semiconductor crystal formation.10,11 An advantage of ec-LLS over the aforementioned methods is the capacity to produce crystalline semiconductor micro/nanowires in aqueous solution at ambient temperatures and pressures.

The preliminary demonstration of ec-LLS was the electroreduction of dissolved GeO2 in aqueous solution at bulk Hg pool electrodes.12 Although the influence of basic ec-LLS parameters (e.g. time, potential, liquid metal type) have since been studied, the size (volume) of Hg electrodes has not yet been directly examined. In contrast to other variables, the Hg pool size should have influence on both the electrochemical and crystal growth aspects of ec-LLS, as both mass transport to the electrode surface and the ratio of the volume of the growing crystallites to the volume of the liquid metal are increased at microdroplets as compared to bulk liquid pools.

We have previously established that liquid Ga droplets with radii of $10^{-7} \text{ m}$ and corresponding volumes of $10^{-15} \text{ cm}^3$ can nucleate single crystalline Ge nano- and microwires.13,14 There are no previous reports on whether the same is achievable with small Hg droplets, i.e. at volumes $10^{10}$ times smaller than our previous investigation with Hg as an ec-LLS electrode/medium.12 The use of Hg microdroplets also presents two additional advantages for study of the ec-LLS process. First, diffusion is fast in such small liquid metal volumes. The diffusivity of Ge in Hg at room temperature has been previously measured as $1.3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$.15 With a radius of $\sim 10 \mu \text{m}$, any dissolved Ge atom at the electrolyte/Hg interface can diffuse the entire volume of Hg in less than 0.04 s. Thus, there is no meaningful time delay in moving Ge into or out of the Hg microdroplet during the respective electroreduction and electrooxidative experiments that last longer than this time. Theoretical calculations of Hg microdroplet radius, $r$, ranging between 5 and 10 $\mu \text{m}$ produce a match with the experimental observations.

Second, small Hg microdroplets support small absolute heterogeneous currents, allowing access to undistorted fast scan voltammetry featuring high current densities. This aspect is not true for macroscopic Hg pool electrodes and was a primary reason why the voltammetry has been difficult to study in concentrated (>10 mM) solutions of dissolved GeO2.16 Accordingly, in this report, Hg microdroplet ultramicroelectrodes with radii, $r$, ranging between 5 and 10 $\mu \text{m}$ are prepared through the conversion of platinum (Pt) ultramicroelectrodes by Hg electrodeposition11 and then used as platforms to attempt Ge ec-LLS. Figure 1 summarizes the scheme employed in this work. The presented data explore three primary hypotheses. First, anodic stripping voltammograms indicate an unexpectedly slow rate of introduction of Ge into Hg through Reaction 1 and a correspondingly small concentration of dissolved Ge in ultra-small volume Hg electrodes.

\begin{equation}
\text{HGeO}_2(aq) + 4e^- + 2H_2O(l) \rightarrow \text{Ge(s)} + 5OH^-(aq)
\end{equation}

Second, the current transient collected during ec-LLS at a single Hg ultramicroelectrode under a constant applied bias tracks the form of the electrodeposited Ge crystal(s). Third, microdroplet liquid metal electrodes yield unique crystalline Ge morphologies relative to the Ge crystals produced with analogous bulk Hg pool electrodes. A series of voltammetric and amperometric data and scanning electron micrographs are presented that address these topics.

**Experimental**

**Materials.**—Pt wire (radius $= 12.5 \mu \text{m}$, 99.95%) was obtained from Alfa Aesar. CaCl2 (97%, Fluka), C2H2O (ACS grade, Fisher), KCl (99%, Sigma-Aldrich), Ru(NH3)6Cl3 (98%, Sigma Aldrich), Hg(NO3)2 (98%, Alfa Aesar), KNO3 (99%, Acros Organics), HNO3 (65% Fisher Scientific), Ar(g) (99.998%, Metro Detroit Welding), GeO2 (99.99%, Sigma Aldrich), and Na2B4O7 (ACS grade, Mallinckrodt) were used as received. Water obtained from a Nanopure II water filtration system with a resistivity > 18 MΩ cm was used throughout.

**Ultramicroelectrode fabrication and use.**—Pt wire was glued onto a small piece of glass slide with cyanoacrylate (Bob Smith Industries), and attached to a variable autotransformer with a voltmeter to control the potential applied. The Pt wire was etched under 4 V in a 20 wt% CaCl2, 1:1 (v/v) water-acetone solution for one minute. The etched Pt microwire was then sealed inside a glass capillary tube via heating with a nichrome heating coil. The sealed end was subsequently filed with sandpaper to expose the Pt wire. Electrical contact to the Pt microwire was made by soldering a copper wire. Scanning electron microscopy was used to determine whether the polishing step exposed a circular microdisk.

Cyclic voltammetry was performed in three electrode cells containing 0.001 M Ru(NH3)6Cl3 and 0.1 M KCl to assess ultramicroelectrode behavior. CH Instruments models 420a and 760c potentiostats were used.
were used throughout. All reported potentials are referenced to a mercury/mercuric sulfate (E(Hg/Hg2SO4)) reference electrode.

Following the protocol of Mauzeroll,17 a solution containing 0.01 M Hg(NO3)2, 0.1 M KNO3, and 0.5% HNO3 was first prepared, purged with Ar(g) for 15 min to eliminate oxygen from the solution, and then kept under an Ar(g) blanket. Hg was then electrodeposited onto the Pt ultramicroelectrode immersed in this solution while biased at −0.1 V for 5 min. The Hg-capped ultramicroelectrode was then transferred to another electrochemical cell containing an Ar(g)-purged solution of 0.05 M GeO2 and 0.01 M Na2B4O7. Ge ec-LLS was then performed via chronoamperometry with an applied potential of −1.94 V for up to 1 h.

Materials characterization.—Scanning electron microscopy was conducted in a FEI Quanta 3D e-SEM/FIB in low vacuum mode with a pressure of 0.60 torr operated at 5.00–10.00 kV, and a FEI Helios 650 Nanolab SEM/FIB operated at 1.00–3.00 kV. Energy dispersive X-ray measurements were obtained using an EDAX 30 mm2 SDD detector. All energy dispersive X-ray data are presented as raw signals, i.e. without any adjustment for differences in relative sensitivities.

Results

Voltammetry.—Figure 2 displays voltammetry illustrating the efficacy of the process to produce Hg ultramicroelectrodes. Figure 2a illustrates the attenuation of the electrocatalytic activity for H+ reduction in 0.01 M Na2B4O7 (aq) following electrodeposition of Hg onto a 10 μm diameter Pt ultramicroelectrode. At a current of 10 nA, the overpotential for H2 evolution increased by nearly 600 mV. The high overpotential was maintained after multiple sweeps, indicating the stability of the Hg microdroplet. The inset to Figure 2 highlights a scanning electron micrograph (top-down view) of a typical Hg microdroplet ultramicroelectrode after preparation. Figure 2b presents a representative cyclic voltammetric response for a Hg microdroplet ultramicroelectrode with r = 8.9 μm in an aqueous solution containing 0.1 M KCl and 0.001 M Ru(NH3)6Cl3. The steady-state current-potential response followed the expected response for a hemispheric ultramicroelectrode.

Figure 3 presents representative cyclic voltammograms for the reduction of 0.050 M dissolved GeO2 in aqueous solution at a Hg microdroplet ultramicroelectrode with r = 8.9 μm. For reference, the standard potential for the HGeO3-/Ge redox couple is −1.34 V.26 The data in Figure 3a were collected at 0.01 V s\(^{-1}\). An increased faradaic current was consistently observed at potentials more negative than −1.7 V when GeO2 was dissolved as compared to the blank electrolyte (Figure 3a). The peak near E = −1.85 V in Figure 3a indicated a transition from kinetic to mass-transport limited current for GeO2 reduction, in contrast to the voltammetric response at a bulk Hg pool electrode in the same ec-LLS electrolyte at a comparably slow scan rate.12 At more negative potentials, the current continued to increase. Although a second peak at E = −2.05 V is apparent in Figure 3a, this feature was not consistently observed. However, a prominent feature that is evident in Figure 3a that was seen in all voltammetric data recorded at this scan rate was the crossover in the forward and reverse scans. The cathodic current was higher at the most negative potential values on the reverse scan, suggestive that the electrode surface was no longer pure Hg after the reduction of dissolved GeO2. Rather, the electrode interface featured some fraction of solid Ge which was more electrocatalytically active for H+ reduction compared with bare Hg. The convolution of the cathodic charge with the electrochemical reduction of H+ precluded direct comparison of the charge passed between the cathodic and anodic sweeps. At more positive potentials, the anodic sweep contained a broad, asymmetric stripping wave beginning at −0.7 V but with a peak potential nominally located at −0.35 V. This anodic stripping peak was consistent with a voltammetric feature reported previously for the oxidation of solid Ge3 at hanging Hg drop electrodes used for the electroanalytical detection of Ge.15,16,21 The unusual asymmetry of the peak shape has been described as arising from both the oxidation of solid Ge at the electrolyte interface and from within Hg.15,16,21

Figure 3b presents separate cyclic voltammograms collected at 10 V s\(^{-1}\) in the presence of dissolved GeO2 at a formal concentration of 0.05 M. In these experiments, a cathodic peak at E = −0.28 V and an anodic wave at E = −0.23 V were routinely observed. Separate

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**Figure 1.** Schematic depictions of (left) the formation of an individual Hg microdroplet ultramicroelectrode via the electrodeposition of Hg onto a glass-encased Pt ultramicroelectrode and (right) the elementary steps in Ge ec-LLS at a Hg electrode.

**Figure 2.** a) Comparison of the voltammetric responses in 0.01 M Na2B4O7 of a Pt ultramicroelectrode before and after electrodeposition of Hg. Scan rate: 0.01 V s\(^{-1}\). Inset: a top-down scanning electron micrograph of a Hg microdroplet ultramicroelectrode. b) Steady-state voltammetric response of a Hg microdroplet ultramicroelectrode immersed in 0.001 M Ru(NH3)6Cl3 and 0.1 M KCl. Scan rate: 0.01 V s\(^{-1}\).
control experiments were performed to confirm these features were neither associated with an unintentional impurity in solution (e.g., contaminants from the electrolyte salt, dissolved O₂) nor related to the underlying presence of Pt below the Hg microdroplet. Instead, these features seemed reminiscent of the formation/removal of polyborate adsorbed layers previously reported on Ag electrodes.22,23 Nevertheless, they do not appear at potentials directly or indirectly associated with the reduction of dissolved GeO₂. The first and tenth scans obtained under these conditions are shown. These two plots are shown to illustrate that some aspects were not constant across multiple scans.

One consistent feature was the absence of a crossover in the forward and reverse scans after the reduction wave for dissolved GeO₂. In both the first and tenth scans, the reduction of dissolved GeO₂ appeared as a typical irreversible cathodic wave without convolution with H₂ evolution, suggesting the electrode interface was still uniformly Hg. The dependence of the peak current with the square root of the respective scan rate from 0.01 V s⁻¹ to 1000 V s⁻¹ was linear (inset), i.e., consistent with the reduction of freely dissolved species in solution rather than adsorbed species. Another common feature in both scans was the absence of a broad anodic stripping wave centered at ∼0.35 V, further indicating solid Ge had not yet formed even though each cathodic wave indicated the production of 5.5 × 10⁻¹⁴ moles of Ge if Reaction 1 was the only operative redox process.

On the first scan, there was minimal anodic current in this potential range. In fact, for all fast voltammetric responses collected, the total anodic charge passed was approximately 20x less than the total cathodic charge passed, particularly since the current at the most positive potentials was broadly in line with the voltammetry for the blank electrolyte shown in Figure 3b. After the first scan, a new symmetric oxidative wave appeared, centered at −0.72 V, and was consistent with the oxidative stripping of dissolved Ge in Hg, i.e., solvated Ge that has not yet phase separated into a solid Ge crystal.15,16 The magnitude of this wave increased with each new scan, until reaching a plateau value by the tenth scan. Assuming this peak is the 2e⁻ oxidation of Ge⁰ dissolved in Ge, a maximum of 4.7 × 10⁻¹⁴ moles of Ge were apparently dissolved within this Hg microdroplet ultramicroelectrode by the heterogeneous reduction of GeO₂. With a total Hg microdroplet volume (assuming a hemisphere as in Figure 2a) of 1.5 × 10⁻⁹ cm⁻³, the effective concentration of Ge in the Hg microdroplet after repetitive scanning was 3.2 × 10⁻³ M (4.74 × 10⁻⁷ mol%). The solubility data for Ge in Hg at room temperature are scattered,24–27 but the most widely cited value is 10⁻⁹ M (10⁻⁷ mol%).28 The data in Figure 3c are thus consistent with the premise that the Hg microdroplet electrodes were not instantaneously but eventually saturated with Ge upon repetitive cycling at fast scan rates.

**Chronoamperometry.**—A total of 35 separate ec-LLS experiments were performed in 0.05 M GeO₂ and 0.01 M Na₂B₄O₇ under constant applied potential. Every ec-LLS attempt yielded a solid Ge deposit that extended outside of the liquid metal ultramicroelectrodes. However, there was notable variation in both the electrochemical data recorded during ec-LLS and the morphology of the electrodeposited Ge produced by ec-LLS, i.e., not every experiment performed under identical conditions yielded the same form of elemental Ge.

Figure 4 illustrates an example of one subset (10 out of 35) of the total experiments. Figure 4a shows the chronoamperometry data for an ec-LLS experiment where a bias of −1.94 V vs E(Hg/Hg₂SO₄) was applied for 1 h. The current decayed slowly until after ~1000 s,
when a steady-state, non-zero current of 2.2 nA was reached. During the first 1000 s, a brief rise in the current was observed. The inset shows the corresponding scanning electron micrograph (top-down view) collected immediately after the completion of the electrodeposition experiment. A round mass was still present on top of the Pt disc ultramicroelectrode but it was not composed purely of Hg. The entire surface of the Hg droplet was covered with a thick shell consisting of elemental Ge, as determined by energy dispersive X-ray spectroscopy (Figure 4b). The Al, Na, Si, and O signals arose from the soda glass and the Hg signal was from the underlying microdroplet. For this subset of samples, the ‘shell’ was granular in appearance but otherwise continuous. For samples where the Ge ‘shell’ was cracked and a cross-sectional view was possible, a thickness of about 300 nm was apparent.

Figure 5 presents data for the other subset (25 out of 35) of ec-LLS experiments attempted with Hg microdroplet ultramicroelectrodes. The current-time profiles for these experiments differed from those shown in Figure 4 in two important ways. First, at long times, the current did not reach the same steady-state value. In fact, the majority of these experiments did not attain any steady-state current, with the measured current increasing over time (Figures 5a, 5c). Second, all of the experiments yielded unique current-time profiles. That is, there were no consistent, identifiable patterns. This latter point corroborated the observations from scanning electron microscopy. As demonstrated in Figures 5b, 5d, the resultant morphology was not a Hg droplet covered by a continuous Ge shell. Rather, the collected data for these experiments showed the extrusion of a coiled microwire. In the previous work of Ge ec-LLS at bulk Hg pool electrodes,12 only large isotropic structures were observed previously in Ge ec-LLS at bulk Hg pool electrodes, and biased at \( E = -1.94 \) V vs \( \text{Hg/Hg}_2\text{SO}_4 \). Additionally, the ‘leaf’ pattern in Figure 6c was oriented along the long axis of the coil. Although the coiled Ge structure appears solid in Figure 6c, a rupture at the midpoint of the coil revealed this feature was not polycrystalline Ge throughout (Figure 6d). Scanning electron micrographs obtained earlier for the same structure at low vacuum (i.e. under conditions where Hg does not evaporate) revealed the core was filled with Hg. As seen in Figure 6d, the interior of the hollow coil featured a highly nodular surface. It was not possible to determine whether the origin of the twisted, hollow coil was an intrinsic (i.e. a specific result from how Ge was nucleated) or an extrinsic (i.e. capillary forces acted upon the Ge tube as it was dried following removal from solution) aspect of this growth. Although the pitch of turns per length was similar between samples, the chirality of the coil was not the same throughout all samples.

**Discussion**

The presented data speak to the following three points. First, electrodeposition of solid Ge\(^0\) is possible at discrete Hg microdroplets. However, the voltammetric responses identified a discrepancy between the amount of Ge\(^2\) that is reduced heterogeneously and the amount of Ge dissolved in Hg and an unexpectedly slow saturation of Hg with dissolved Ge. Second, the current transients collected during electrochemical ec-LLS experiments with these platforms provide some information on the resultant morphology of the Ge crystals. The limited correlations between the current transients and resultant Ge morphologies argue against precise, real-time feedback control during this type of ec-LLS. Third, the crystalline Ge produced during ec-LLS has different structural characteristics when performed similar to what was observed at bulk Hg electrodes after Ge ec-LLS was performed at low overpotentials.12 Figure 6c presents a high magnification view of a section of the coil. The surface was highly textured but distinct from that shown in Figure 6b. Here the surface presents solid Ge with a branched, ‘leaf’-type pattern. Again, a similar pattern was observed previously in Ge ec-LLS at bulk Hg pool electrodes, but only at moderate to large overpotentials.12 Additionally, the ‘leaf’ pattern in Figure 6c was oriented along the long axis of the coil. Although the coiled Ge structure appears solid in Figure 6c, a rupture at the midpoint of the coil revealed this feature was not polycrystalline Ge throughout (Figure 6d). Scanning electron micrographs obtained earlier for the same structure at low vacuum (i.e. under conditions where Hg does not evaporate) revealed the core was filled with Hg. As seen in Figure 6d, the interior of the hollow coil featured a highly nodular surface. It was not possible to determine whether the origin of the twisted, hollow coil was an intrinsic (i.e. a specific result from how Ge was nucleated) or an extrinsic (i.e. capillary forces acted upon the Ge tube as it was dried following removal from solution) aspect of this growth. Although the pitch of turns per length was similar between samples, the chirality of the coil was not the same throughout all samples.
with Hg microdroplets or Hg bulk pool electrodes. These points are elaborated individually below.

**Observations from voltammetry.**—The voltammetric data here implicate an unexpectedly slow accumulation of Ge inside Hg. Specifically, the data collected here identify a large discrepancy between the cathodic and anodic charges passed that is not related to the competing evolution of H₂. The much greater cathodic charge passed during the reduction of dissolved GeO₂ in fast scan voltammetry unambiguously shows that only a small fraction of the reduced product results in Ge⁰ dissolved in Hg. Although the linear dependence of the peak current on the square root of the scan rate is consistent with the reduction of a GeO₂ species dissolved in the aqueous electrolyte rather than adsorbed on the electrode surface, the possibilities of (1) additional redox processes occurring in parallel with Reaction 1 at negative applied potentials, (2) undefined coupled chemical reactions that eliminate any freshly produced Ge⁰ at the electrode surface, (3) the transient formation of a redox inactive Ge-Hg compound, or (4) the 4e⁻ reduction of GeO₂ forming a soluble Ge²⁺ intermediate that diffuses away sufficiently fast to yield inefficient production of Ge⁰ cannot be ruled out. For example, dissolved GeO₂ could get hydrogenated to form a hydride (e.g. GeH₄)³⁰ with transient stability in solution. Such a parallel redox process would naturally lower the faradaic efficiency for crystalline Ge formation. Although the generation of Ge hydrides electrochemically has been studied previously, the prevailing sense is this type of hydrogenation is slow and never proceeds with high faradaic efficiency at metal electrodes.³⁰ The rate of Ge hydride formation at Hg has not been previously reported. A separate possibility is that Ge⁰ is produced at the Hg interface but then desorbs (oxidatively) into solution faster than the rate of dissolution into Hg. The third possibility is that Ge and Hg form a metastable and electroinactive intermetallic species. There is no known precedent for such a compound. In contrast, the formation of a Ge²⁺ intermediate is plausible,¹⁵,¹⁶ but substantiation requires a more detailed understanding of the GeO₂ electroreduction process, the reactivity and stabilities of all intermediates, and their diffusivities. Such work is ongoing in our laboratory.

**Observations from chronoamperometry.**—The current-time data contained some useful information on the initial nucleation and crystal growth during ec-LLS. The slow current decay and peak indicated that Ge electrodeposition occurred over the first 1000 s. After that point, a time-independent current was useful in predicting if a continuous Ge coating was formed. We posit that a continuous Ge shell effectively stopped further Ge ec-LLS, as the electrodeposition of Ge on Ge is not possible under the employed conditions.³⁰ The residual current was likely from some non-zero rate of H⁺ reduction on Ge at the applied potential. Conversely, if the current rose slowly over time after the first 1000 s, a pierced/broken/discontinuous Ge shell was routinely observed. In that aspect, the current-transients were consistent. However, for these ec-LLS experiments, both the current transients and the corresponding Ge deposits were unique and without any discernible patterns. Nothing in the current-time profiles seemed to indicate how or when the Ge nanofilament bundles were extruded. Additionally, there were no apparent periodic oscillations in the chronoamperometry data that followed the periodicity of the twists in the Ge nanofilament bundles. As a result, these data do not support the premise that a simple analysis of the current-time transient in an ec-LLS experiment is a precise indicator of the morphology of the solid that is produced when a Hg microdroplet is used.

With regards to formation of crystalline Ge, the results shown here with Hg microdroplets illustrate some important similarities and differences to liquid Ga and Ga-In alloy liquid metal microdroplet electrodes.¹³,¹⁴ In general, the data shown here further emphasize that ec-LLS can be a synthetic method at the micro-, meso-, and macro- length scales. However, with liquid Ga or Ga-In microdroplets, the growing Ge crystal(s) push the liquid metal nano/microdroplet away from the surface because nucleation and crystal growth occur preferentially at the interface between the liquid metal droplet and the support substrate. Accordingly, such ec-LLS experiments necessarily involve a moving boundary as the position of the active electrode interface changes with time. In contrast, none of the trials in this work yielded a Hg microdroplet pushed away from the underlying Pt microdisk substrate. Instead, the data all are in line with Ge extruding out of the Hg microdroplet, perhaps because Ge nucleated and grew from inside Hg rather than at the interface between Hg and Pt.

The Hg microdroplet remained attached to the Pt ultramicroelectrode throughout the electrodeposition processes shown here. Strong adhesion of the Hg microdrosplets on Pt are in line with the finite solubility of Pt in Hg at room temperature (10⁻⁹ mol% at T = 25 °C).³¹ The possibility exists that heterogeneous nucleation specifically prevented the heterogeneous Ge nucleation and crystal growth observed previously with Ga microdroplets. To explore this point further, additional ec-LLS experiments were performed with Hg microdroplets electrodeposited on a degenerately doped n⁺-Si wafer since there is no metallurgy or wetting of Hg on Si at T = 25 °C.²⁵ For these experiments, there was no possibility of an amalgam forming that could prevent heterogeneous Ge nucleation and growth. After ec-LLS experiments, none of these Hg microdroplets were displaced away from the substrate, arguing against an amalgam adhesion layer as the reason the Hg microdroplet remained in contact with the Pt ultramicroelectrode during ec-LLS. Instead, these data implicate some specific property of Hg itself as the reason why heterogeneous nucleation did not occur as has been observed previously with other types of liquid metal microdroplets. One property that could have a strong influence is the solvent power of the liquid metal. The solubility of Ge in Hg is 10,000 times less than Ge in Ga at T = 25 °C (10⁻⁷ mol% vs 10⁻³ mol%, respectively).³¹,³² Based on this fact alone, Ge crystal nucleation and growth should start sooner in Hg than Ga during a set of otherwise identical ec-LLS experiments, perhaps making it difficult for crystal growth to occur far from the liquid metal/electrolyte interface when Hg is used.

**Comparison of Ge ec-LLS at micro and macro liquid Hg droplets.**—This work indicates several clear distinctions between ec-LLS experiments with Hg microdroplets and bulk Hg pools. First, in our past work with bulk pool Hg electrodes, cessation of Ge ec-LLS by the formation of a continuous solid shell never occurred. That is, the amount of Ge deposited always tracked with charge passed and was unabated over long times (≥ 8 h). In contrast, ec-LLS experiments with the Hg microdroplet ultramicroelectrodes here showed a substantially higher probability for the formation of a solid Ge shell that precluded deposition at long times. To be clear, a Ge shell was also observed with bulk Hg pool electrodes, but the distinction was that it served as a nucleating point for polycrystalline Ge nanowires but never fully encapsulated the bulk Hg pool.

The data indicated that Ge ec-LLS involves a compressive force on the liquid metal that can disrupt the initial Ge shell. It is presently unclear whether that force is more prominent at a macroscopic Hg electrode interface, but the data suggest a pathway for ‘fresh’ Hg to remain in contact with the electrolyte solution. Accordingly, it seems the probability that such events could scale with surface area and thus be the reason why ec-LLS at large Hg pool electrodes is always continuous.

Second, the compression of the liquid Hg, in conjunction with the small finite volumes, also facilitated the deposition of unique Hg-filled Ge microtube structures that were never observed with bulk Hg pool electrodes. In fact, such morphologies have not been observed in any other electrodeposition context, ec-LLS or otherwise. Although there might not be an immediate application for the specific hollow Ge structures prepared here, the data shown in the report illustrate the unusual and unexplored concept of using compressed liquid metal electrodes to form unique hollow structures. Accordingly, this phenomenon could be exploited purposefully in the future to synthesize electrochemically hollow micro- or macrostructures.
Conclusions

In this work, small Hg microdroplet ultramicroelectrodes facilitated Ge ec-LLS through the reduction of aqueous solutions of dissolved GeO$_2$. The voltammetric data suggest a complex interplay between the reduction of dissolved GeO$_2$ and the dissolution of Ge into Hg. Chronoamperometric experiments showed the formation of continuous Ge shells, an observation never seen before in ec-LLS with either large volume Hg electrodes or similarly sized Ga microdroplet ultramicroelectrodes. The formation of Hg-filled, crystalline Ge coil structures at long times was unprecedented and suggests the possibility of synthesizing unique hollow structures by electrodeposition.

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