Humidity Effect on Nanoscale Electrochemistry in Solid Silver Ion Conductors and the Dual Nature of Its Locality

Sang Mo Yang, Evgheni Strelcov, M. Parans Paranthaman, Alexander Tselev, and Sergei V. Kalinin

*Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 151-747, Korea
†Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea
‡Center for Nanophase Materials Sciences and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Supporting Information

ABSTRACT: Scanning probe microscopy (SPM) is a powerful tool to investigate electrochemistry in nanoscale volumes. While most SPM-based studies have focused on reactions at the tip–surface junction, charge and mass conservation requires coupled and intrinsically nonlocal cathodic and anodic processes that can be significantly affected by ambient humidity. Here, we explore the role of water in both cathodic and anodic processes, associated charge transport, and topographic volume changes depending on the polarity of tip bias. The first-order reversal curve current–voltage technique combined with simultaneous detection of the sample topography, referred to as FORC-IVz, was applied to a silver solid ion conductor. We found that the protons generated from water affect silver ionic conduction, silver particle formation and dissolution, and mechanical integrity of the material. This work highlights the dual nature (simultaneously local and nonlocal) of electrochemical SPM studies, which should be considered for comprehensive understanding of nanoscale electrochemistry.

KEYWORDS: Humidity, electrochemistry, silver, ionic conduction, locality, scanning probe microscopy

Electrochemistry in nanoscale volumes is important for current key research in material science, chemistry, and physics, including energy conversion and storage, catalysis, and environmental sciences.\(^1\)–\(^12\) It also underpins many applications, including memristors,\(^3\)–\(^4\) bias-induced nanofabrication,\(^5\) atomic switches,\(^6\) and inorganic synapses for future neuromorphic systems.\(^7\) However, our understanding of electrochemical processes in nanoscale volumes remains limited because the processes occur in limited spatial and temporal domains and can have unusual mechanisms, making nanoscale manipulations challenging.\(^5\) Additionally, the processes are strongly affected by the complexity of electronic and/or ionic transport, as well as strain fields and mechanical effects.\(^8\)

Scanning probe microscopy (SPM) provides a unique opportunity to investigate local electrochemical phenomena and associated charge transfer at the nanoscale, such as the recently developed first-order reversal curve current–voltage (FORC-IV) method\(^9\)–\(^10\) and electrochemical strain microscopy (ESM).\(^11\)–\(^14\) In FORC-IV and ESM, the conductive SPM tip with a nanometer-sized apex confines the electric field to a small volume of material, thus simultaneously activating electrochemical reactions and detecting the signatures of electrochemical changes via force, current, and/or mechanical displacement. In addition to local electrochemical probing, SPM allows for manipulation of physical and chemical properties of the material at the nanoscale. A typical example is tip bias-induced nanofabrication, also referred to as scanning probe lithography.\(^5\) A confined electric field and/or associated current lead to either a locally controlled deposition or growth of material on a surface. This characteristic can be applied as the operation principle of advanced electronic nanodevices, for example, silver particle deposition and its dissolution for atomic switches\(^9\) and inorganic synapses.\(^7\)

Traditionally, in SPM-based local electrochemical probing and engineering, the interest is focused on the processes at the tip–surface junction rather than that at the counter interface (normally a large bottom electrode). The reaction localized under the tip and accompanying changes, including the changes of topographic volume, surface potential, and/or contact resonance frequency, are the main concern, but the reaction at the counter interface is often overlooked in the tip-induced electrochemistry studies.\(^15\)–\(^16\) However, charge and mass conservation always requires coupling between the cathodic and anodic processes, and either of the half reactions can be the limiting step of the overall process. This is indicative of the intrinsic nonlocality of the electrochemical process, although SPM seemingly probes a nanoscale volume locally, immediately beneath the tip.

Received: October 20, 2014
Revised: December 25, 2014
Furthermore, ambient water (humidity) can have a strong effect on this nonlocal cathodic–anodic coupling. Recently, the effect of moisture on electrode redox reactions and cationic transport in electrochemical metallization (ECM) cells (cationic conductors sandwiched between electrochemically active and inert electrodes, i.e., capacitor geometry) has been reported. Moisture presence in these systems leads to the change of resistive switching properties. Specifically, the recent review by Valov discussed in detail the coupling between the two half-cell reactions and effect of moisture in the redox-based resistive switching memories. In SPM experiments, water typically provides an active medium for charge transfer and confines the reaction laterally due to the size of its meniscus. However, electric bias is usually applied until some detectable response is achieved, which can correspond to a serendipitous half reaction such as ambient water dissociation or oxidative water splitting. Those processes yield proton (H+) or hydroxyl ion (OH−), which can participate in unwanted half reactions, so they can affect both cathodic and anodic processes, their chemical reversibility, associated conduction, and electrochemically driven topographic changes in the materials. Therefore, the effect of humidity on the nonlocal cathodic and anodic processes on both interfaces should be examined to increase our understanding of electrochemistry in nanoscale volumes.

Here, we explore the effect of water on electrochemical redox processes, associated charge transport, and topographic volume changes at the nanoscale depending on the polarity of tip bias. We combined humidity-dependent FORC-IV measurements with simultaneous monitoring of the sample surface height change, referred to as FORC-IVz, to investigate nanoscale electrochemistry in a solid silver ion conductor, which is a simple system that has been well-characterized in bulk. We examine the role of water on silver ion conduction, silver particle formation and dissolution, chemical reversibility of processes, and mechanical integrity of the material. The dual nature of electrochemical SPM studies, that is, local SPM probing of intrinsic nonlocality of the coupled cathodic and anodic processes, is also discussed.

As a model system for this study, we chose AgI-based solid ion conductors, (AgI)0.20(Al2O3)0.05(AgPO3)0.75 glasses, prepared using a melt-quenching method (see Supporting Information, Section 1). (AgI)x(AgPO3)1−x conducting glasses are classic solid electrolytes with highly mobile Ag+ ions. Their conductivity reaches about 10−2 S/cm for the 60 mol % AgI containing glass, that is, comparable to the liquid electrolytes. Ag-ion solid electrolytes provide a good model system for measuring electrochemically driven topographic changes, since they are more chemically stable in air compared with other electrolytes, such as Li-ion conductors.

More importantly, they have recently attracted considerable attention as materials for advanced electronic nanodevices, including memristive ECM cells, atomic switches, and inorganic synapses. Thus, there have been extensive SPM studies on Ag-ion conductors, performed by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). It is worth noting that STM enables much higher spatial resolution, even down to atomic scale, and single atomic contact for investigating atomic switches. However, for this humidity-dependent FORC-IVz study, we have chosen AFM to detect the current through the sample and the height change of the sample surface simultaneously. AFM can measure independently both current and force at the same time, whereas STM measures only (tunneling) current. Hence, AFM allows for measuring IVz spectra that provide the information on both electrochemically driven volume change and charge transfer. In STM, to detect Δz the constant-current mode should be performed, whereas to monitor current, the constant tip–sample distance mode should be used. In addition, STM is typically performed under ultrahigh vacuum condition; thus, it is limited with respect to accessible humidity range. On the other hand, AFM allows us to easily control humidity in a much wider range, for example, from 0 to 90% relative humidity (RH), as performed here.

FORC-IVz measurements were performed on Multimode (Bruker) AFM interfaced with a National Instrument card controlled by the Labview/Matlab software. The FORC-IV method is based on the local I–V measurement and employs a bias waveform composed of a sequence of triangular pulses with increasing amplitudes. By monitoring the I–V hysteresis loop opening, which is proportional to the local electrochemical activity, it is possible to differentiate between ionic and electronic transport in materials. A schematic of the experimental setup is illustrated in Figure 1a. The Pt/Cr-coated AFM tip (Budget Sensors, Multi75E-G) and silver paste bottom electrode can be considered electrochemically inert and active metal electrodes, respectively. To limit current flow and eliminate run-away reactions leading to considerable large-scale topographic changes, a 1 GΩ protective resistor was connected

![Figure 1](image-url)
in series with the sample. The current through the sample was measured using a commercial current amplifier (Femto, DLPCA-200). Experiments were performed at room temperature and at various RH ranging from 0 to 90%. For the 0% RH measurements, we preheated the sample at \( \sim 110 ^\circ \text{C} \) for 30 min under dry air flow. The variable humidity measurements were enabled by controlling the water content in air in the AFM cell using a General Electric MG110 hygrometer calibration tool. Image and data processing were performed using WSxM\(^{39}\) and custom-written Matlab codes, respectively.

We first performed FORC-IVz measurements by applying a negative tip bias waveform (Figure 1b) at 0% RH. Figure 1c shows \( I-V \) curves averaged over 100 measurements of the 10 \( \times \) 10 grid on a 15 \( \times \) 15 \( \mu \text{m}^2 \) region. The grid was used to obtain statistically significant information and explore the behavior reproducibility. Bias application led to the formation (at \( \sim -0.2 \) V) and subsequent growth of silver particles beneath the AFM tip. Simultaneously, a hysteretic \( I-V \) curve response was detected that gradually transformed into a closed linear response with a total resistance of \( \text{dV/dI} \sim 1.07 \text{ G} \Omega \) (i.e., protective resistor-limited current) as the pulses with higher peak bias were applied. Note that almost identical \( I-V \) curves were observed at other RH (Supporting Information, Figure S1). This suggests that water does not play a critical role in conduction at negative tip bias.

The flow of current at negative tip bias can be explained in terms of interfacial Faradaic Ag redox processes and Ag\(^+\) ion transport without considering the involvement of water. Upon application of a negative bias to the tip (the source of electrons e\(^-\)), Ag\(^+\) ions are drawn toward it. When a critical potential is exceeded, the cathodic silver reduction process

\[
\text{Ag}^+ + e^- \rightarrow \text{Ag(s)} \quad (1)
\]

takes place at the tip–surface junction and silver metal particles are formed on the glass surface beneath the tip, leading to an increase in local topography. Simultaneously, the counter anodic half-reaction of silver oxidation (or dissolution)

\[
\text{Ag(s)} \rightarrow \text{Ag}^+ + e^- \quad (2)
\]

occurs at the Ag bottom electrode (the silver reservoir), which maintains the electroneutrality of the sample. Hence, the cationic current of Ag\(^+\) flows inside the glass. As can be seen in eqs 1 and 2, water does not participate in the cathodic and anodic reactions. Hence, similar \( I-V \) curves were observed at all RH values. A schematic of the electrochemical processes at negative tip bias is illustrated in Supporting Information, Figure S2.

To characterize the nature of the observed current we compared the area under the \( I-t \) curve (transferred charge) and the volume of deposited silver particle (Supporting Information, Section 2.3). This yielded a transference number of unity for Ag\(^+\) cations in the glass (i.e., no electronic conduction). It is worth noting that the total potential drop represents the sum of the overpotentials of Ag reduction, dissolution, and IR drop due to the resistances of the tip (presumably negligible), sample (i.e., spreading resistance), and protective resistor. However, the Ag dissolution overpotential is negligible due to the large area difference between the tip and the counter electrode,\(^{20}\) and the IR drop is huge in this system due to the protective resistance of 1 G\(\Omega\) and large spreading resistance (roughly 0.1–10 G\(\Omega\) depending on the radius of the deposited silver particle,\(^{28,33}\) see Supporting Information, Section 2.4). Thus, the Ag reduction overpotential is quite small (below \( -0.2 \) V). In addition, we found that local Joule heating effect is negligible in this system (Supporting Information, Section 2.5).

Figure 1d shows average absolute and relative FORC \( I-V \) loop areas as functions of the peak bias at 0% RH. The relative loop area is proportional to the local electrochemical activity.\(^9\) This was calculated based on the normalization using the square of the peak bias divided by the protective resistance.\(^10\) The average absolute loop area increased with the peak bias, while the average relative loop area decreased to almost zero (Figure 1d). The electrochemically driven height change, \( \Delta z \), also showed a strong correlation with the relative FORC \( I-V \) loop area since both are proportional to the local electrochemical activity (Figure 1e). The change in positive \( \Delta z \) (i.e., the protrusion of silver on the glass surface) decreased down to almost zero with increasing the peak bias. Because the transference number for Ag\(^+\) cations in the glass is almost unity, we cannot consider the electronic conduction in the glass. Therefore, the lack of loop opening at the high peak bias is likely due to the protective resistor limiting the current and masking the loop opening. In addition, the negligible \( \Delta z \) indicates that the silver particle growth mode transits from vertical growth mode to lateral, as observed in the particle geometry. We observed that \( \Delta z \) was weakly reduced with increasing RH during the initial stages (Figure 1f). This can be explained by the water meniscus formation at the tip–surface junction, which decreases the applied field strength.

Having discussed the insignificant effect of water at the negative tip bias polarity, we performed humidity-dependent positive bias FORC-IVz measurements. We used the same size of a 10 \( \times \) 10 grid and the bias waveform illustrated in the inset of Figure 2a. Interestingly, we observed that the current did not flow at 0% RH (Figure 2a), whereas it flowed at other RHs (Figure 2b–d). Only a negligible current of about a few picoamperes was detected at 0% RH, which was attributed to the capacitance of the sample. Because the glass initially contains mobile Ag\(^+\) ions, a minute current can flow until the polarization process (i.e., charge separation) is completed and the external electric potential is almost canceled inside the sample. However, a large steady-state current flowed only under nonzero humidity, indicating that the presence of water is essential for conduction at positive tip bias, contrary to the negative tip bias.

Application of a positive bias to the tip leads to depletion of Ag\(^+\) ions in the sample underneath the tip with simultaneous increases in Ag\(^+\) concentration at the counter bottom electrode (polarization process). The migrated Ag-ions may further discharge at the bottom electrode according to eq 1, when a critical potential is exceeded (Faradaic process). However, in order for the cathodic Ag reduction reaction to continue at the bottom electrode, the counter anodic reaction must proceed at the tip–surface junction neutralizing the charge of the formed Ag\(^+\) vacancies in the vicinity of the tip. The importance of this counter reaction was also noted in the ECM cells, which cannot operate unless a Faradaic process takes in run at the counter electrode.\(^{17–20}\) The Pt/Cr-coated tip is an ion-blocking and electrochemically inert electrode, and a silver reservoir does not exist at the tip–surface junction. Thus, to balance the excessive negative charge at the anode, another source of counter charge is required. At 0% RH the only candidate for the anodic reaction at the tip–surface junction is oxidation of iodine anions (I\(^-\)) in the sample, because Ag\(^+\) ions are mobile only in the AgI regions and not the AgPO\(_3\) regions.\(^27\) However, at
room temperature and the used field strengths iodine anions are immobile in this system.\textsuperscript{41} Hence, the failure of the counter charge transfer reaction at the tip–surface junction results in blocking of the cathodic processes at the bottom electrode.\textsuperscript{17–20} Thus, zero steady-state Faradaic current is detected at 0% RH for positive tip bias.

This reveals the inherent dual nature of electrochemical SPM measurements. SPM probes the local electrochemical process occurring at a nanoscale volume beneath the tip. However, at the same time this process depends on the counter reaction that occurs a large distance from the tip. Unlike the local component, the nonlocal component of the response does not vary with the tip position. However, it still exerts much of a control on the measurements and should be considered to understand electrochemical processes in nanoscale volumes.

On the other hand, an active counter-reaction is possible under ambient conditions, where atmospheric water can supply the counter charge according to the anodic oxidation reaction given by

\begin{equation}
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+ + 4\text{e}^-(3)
\end{equation}

Therefore, the presence of water is required for continuous Faradaic current at positive tip bias. The critical role of water to supply the counter charge for enabling the whole electrochemical process was also discussed in the ECM cells.\textsuperscript{17–20} A schematic of the electrochemical processes at positive tip bias is illustrated in Supporting Information, Figure S5.

In addition to enabling the continuous Faradaic process, the presence of water enhances the conductance in the glass. As RH increased, the total resistance (\(dV/dI\)) of the initial state decreased and the current value at the peak bias increased (Figure 2e). The origin of the enhanced conductance may be the result of another ionic species involved in the conduction, as discussed below. At positive tip bias, the current increased during the forward potential sweep and returned to the low-current state during the reverse potential sweep. After the glass returned to the low-current state, a negative current flowed even though a positive bias was still applied to the tip. As a result, the \(I–V\) curve did not cross the origin. This nonzero-crossing \(I–V\) behavior was also observed in the negative bias FORC-IV\textsubscript{z} measurements. The nonzero-crossing \(I–V\) characteristic reveals that our system has inherently nonequilibrium states, as recently reported by Valov et al.\textsuperscript{4} Thus, we can consider our Ag-ion conducting glass as a nanobattery.\textsuperscript{30} The application of negative and positive tip biases correspond to the charging and discharging processes in a battery, respectively.

To further investigate the electrochemical activity, we calculated the area of the FORC-IV\textsubscript{z} loop opening. We found that the \(I–V\) curves at the positive tip bias polarity can be analyzed by two subloops, which are divided by the cross point (Figure 2b, inset). The first subloop is defined as the closed curve before the cross point and the second is that after the cross point. The value of the cross point voltage increased with RH (for 90% RH, it was located at \(\sim1.85\) V). As shown in Figure 2f, the total subloop area, the sum of the first and second subloops, increased with RH at low peak biases (1.1 and 2 V), but it seemed to be saturated at all RH values at high peak bias (3 V). Interestingly, the first subloop area was dominant in the total subloop area at 90% RH, whereas the second subloop area was prominent at 30% RH. Namely, the first subloop area increased with increasing humidity. Therefore, the electrochemical reaction initiates and becomes more active at a lower bias with higher humidity conditions.

Topographic images recorded after the positive bias FORC-IV\textsubscript{z} measurements show the formation of holes, presumably due to electromigration of Ag\textsuperscript{+} ions and associated transformation of material underneath the tip (Figure 3a–c). Interestingly, the decrease of height (i.e., the hole depth) reduced with increasing RH (Figure 3d), although the total transferred charge (the area under \(I–t\) curve) increased with increasing RH. This cannot be explained by silver-ionic motion alone, implying that another ionic species (other than the Ag\textsuperscript{+} ion) should play an important role in conduction at positive tip bias.

We suggest that the protons generated by oxidative water splitting participate in the conduction as another mobile ionic species.\textsuperscript{19,20} Because of its small size and positive potential of the tip, H\textsuperscript{+} can migrate into the sample, resulting in proton conduction. Then, two possible scenarios can be realized at positive tip bias and humid atmosphere depending on experimental parameters: (i) protons are generated in the water meniscus at the tip–surface junction (eq 3) and migrate into the glass displacing Ag\textsuperscript{+} ions that move to the bottom electrode and discharge (eq 1); or (ii) the generated protons have sufficient mobility in the glass and enough time during bias sweeps to reach the bottom electrode and discharge (i.e., 2H\textsuperscript{+} + 2e\textsuperscript{−} \(\rightarrow\) H\(_2\)(g)) parallel to Ag\textsuperscript{+} reduction. However, the sample thickness was about 2.5 mm and the FORC pulse with largest peak bias lasted for about 2 s (the forward potential sweep). Thus, the proton diffusivity can be roughly estimated as
3 mm$^2$/s. Considering the typical proton diffusivity in water of $\sim 10^{-2}$ mm$^2$/s,$^{42}$ this large estimated diffusivity value excludes the second scenario. Therefore, the generated protons must replace silver ions in the glass beneath the tip, not having time to migrate any deeper. This partial substitution of H$^+$ in the vicinity of the tip–surface junction can explain the aforementioned conductance enhancement in terms of simple series resistor model. The region where protons exist seems to be more conductive. Since such region is thicker at higher RH, the conductance becomes larger at higher RH, too.

It can be speculated that the substitution of Ag$^+$ with H$^+$ in the glass preserves the material’s integrity better than simply depleting it of Ag$^+$ ions, because the latter case is associated with a strong repulsion of the lattice anion groups (I$^-$ and/or PO$_4^{3-}$) due to uncompensated negative charge. This repulsion may lead to mechanical softening of the glass beneath the tip and hole formation. The glass softening can be checked by the shift of contact resonance frequency during an application of bias, because the contact resonance frequency is very sensitive to the tip–surface contact.$^{31}$ As shown in Figure 3e, the resonance frequency shows a rapid jump by $\sim 10$ kHz in a very narrow bias interval (0.5 V) for a bias of $\sim 0.9$ V, which is similar to the onset voltage for the current increase and the hole formation; that is, the onset of reaction. This rapid resonance frequency shift is indicative of a change in the elastic properties of materials and/or adhesion induced by the glass softening and hole creation. The substitution of Ag$^+$ with H$^+$ could mitigate these processes. The generated proton concentration is proportional to humidity, thus less softening and a shallower hole are expected at higher RH. Therefore, the involvement of H$^+$ as a mobile ion species can explain not only the enhancement of conductance but also the decrease in height reduction with RH.

Finally, we investigated the reversibility of the electrochemical silver redox processes using bipolar FORC-IVz measurements. We first examined at 0% RH to rule out the complicated effect of water. Figure 4a shows the applied bias waveform and current response averaged over the entire grid. The first three positive triangular pulses were used for highlighting the lack of conduction at positive tip bias without water. The current started to flow only when the first negative bias pulse was applied (the open arrow). This demonstrates clearly that water is not required for conduction at the negative tip bias polarity. Interestingly, following the first negative bias pulse, the current flowed during the next positive pulse (the solid arrow), even though the peak bias of the applied pulse (1.2 V) was smaller than that of the previous three positive pulses (2.1 V). This positive current suggests that the silver particle, which formed on the glass surface during the application of a negative pulse, dissolved reversely. In other words, the silver redox processes on the glass surface is chemically reversible; thus, the Faradaic current at positive tip bias is feasible even at 0% RH. Here, it should be noted that we do not mean the process is “electrochemically reversible”, indicating that the electron transfer occurs quickly without significant thermodynamic barriers.$^{43}$ In the remainder of this paper, we will use “reversible” as the meaning of “chemically reversible”.

Time-dependent silver particle height changes show unambiguously that the silver redox process is reversible. The average $\Delta z$–$t$ curve exhibited alternating increases and decreases in the particle height corresponding to the negative and positive pulses, respectively (Figure 4b). However, the average $\Delta z$ did not return to zero, indicative of the partial reversibility of the processes. Contrary to the average behavior, the individual local current and height change exhibits high variability depending on the position. Figure 4c shows topography image recorded after the bipolar FORC-IVz measurement. The residual silver particles with an intrinsic dendrite shape were observed at many points with various sizes. Interestingly, no silver particles were observed after the measurement at a few points like point A in Figure 4c. Figure 4d shows that $\Delta z$ returned to the initial zero in point A. This suggests that a fully reversible Ag redox process occurred.

![Figure 3](image-url) **Figure 3.** Topographic images recorded after the positive bias FORC-IVz measurements at different RH: (a) 30%, (b) 60%, and (c) 90%, showing the formed holes. All image sizes are 17 × 17 μm$^2$. Scale bar in (c) is 3.4 μm. (d) $\Delta z$–$t$ curves averaged over the points of a 10 × 10 grid at different RH. (e) (top panel) Single point two-dimensional ESM amplitude spectrogram averaged over the points of a 5 × 5 grid, as measured under the ambient environment. (bottom panel) The arrows existed before the measurement. (d) Single $I$–$t$ and $\Delta z$–$t$ curves measured at point A.

![Figure 4](image-url) **Figure 4.** Bipolar FORC-IVz measurements. (a) The bias waveform for the measurement and $I$–$t$ curves averaged over the points of a 10 × 10 grid measured at 0% RH (b) Average $\Delta z$–$t$ curves. (c) Topography image recorded after the bipolar FORC-IVz measurement. The image size is 17 × 17 μm$^2$. Scale bar is 3.4 μm. Note that the bottommost row was not scanned in the image and the defect site indicated by the arrow existed before the measurement. (d) Single $I$–$t$ and $\Delta z$–$t$ curves measured at point A.
full reversibility of electrochemical processes is essential and is a key factor limiting the electrochemical device’s successful deployment.\textsuperscript{30}

The reversibility of the silver redox process should be dependent on the applied bias waveform. To get further insight into the full-reversibility of the silver redox processes, we used a simple pulse chain composed of five equal bipolar pulses (Figure 5b), similar to those employed in cyclic voltammetry. We observed only a few residual large particles after the measurement (Figure 5a), contrary to the previous bipolar FORC-IVz measurement. However, crater-like small topographic features were observed in almost every position (also see Supporting Information, Figure S6). The central depressions in the crater features must have formed during the dissolution process, occurring at the center of the formerly deposited silver particles where contact with the tip was most intimate. However, the outskirts of the particles seem to have lost electrical contact with the tip (electrode) during the dissolution process, thus being excluded from the following redox reactions. We emphasize that these residual silver craters were due to the loss of electrical/mechanical contact with the tip, and not the low reversibility (or irreversibility) of the electrochemical silver redox processes. This indicates that the lateral size of silver particles compared with the tip radius is a limiting factor for the fully reversible silver redox process. Schematics of the electrochemical processes at bipolar pulses are illustrated in Figure 6. Because the tip measures topography in a small area just beneath its apex (where the contact was best), ensuring high reversibility of the process, the average Δz−t curve shows a fully reversible particle growth (Figure 5b).

Figures 5c shows the spatial map of the residual particle height measured by the tip. Point A, indicated by the open circle, is the site where the residual particle was in the outskirts region (Figure 5a); thus, it was not detected by the tip.

The I−V curves contain information on all aspects of the silver electrochemical process, both reversible and irreversible, as incomplete dissolution of silver particles in outskirt regions would be reflected by asymmetry of the I−V hysteresis loops at opposite polarities. The average I−V hysteresis loops show an extended-memristive behavior\textsuperscript{4} with the aforementioned non-zero-crossing I−V characteristics (Figure 5d). They are shown as a single curve, but we note that the first cycle was different due to the initial particle formation and the other four cycles overlapped. We calculated the total negative and positive relative loop areas (denoted by $R_{N}$ and $R_{P}$) at each pixel, indicative of the extent of local electrochemical activity of the silver particle formation and dissolution, respectively (Figures 5e,f). The difference between $R_{N}$ and $R_{P}$ that is, $R_{N} - R_{P}$ should be proportional to the size of the residual silver particle.

The value of $R_{N} - R_{P}$ averaged over the whole grid was about

**Figure 5.** (a) A topography image after a bipolar FORC-IVz measurement at RH 0%. The image size is 17 × 17 μm\textsuperscript{2}. Scale bar is 3.4 μm. Note that the topography at (1,1), indicated by the arrow, was not scanned in the image and the vertical scale is oversaturated to show the crater features. (b) The bias waveform used for the measurement and Δz−t curves averaged over the whole grid. (c) Spatial maps of the measured residual particle height. (d) Average I−V curves. The total relative loop area maps, summing the relative I−V loop areas of five (e) negative and (f) positive pulses, denoted by $R_{N}$ and $R_{P}$ respectively. Spatial maps of (g) the difference ($R_{N} - R_{P}$) and (h) the difference normalized by $R_{ij}$ i.e., ($R_{N} - R_{P}$)/$R_{ij}$.

**Figure 6.** Schematics of the electrochemical processes at bipolar pulses. (a) Upon application of a negative bias to the tip, silver particles formed beneath it. (b) When applying a positive bias to the tip, the particle starts to dissolve and the tip plunges in. (c) After the outskirts of the particles lost electrical contact with the tip during the dissolution process, the regions cannot dissolve; thus, the silver crater remains. (d) Schematics of I−V and Δz−V curves corresponding to the electrochemical processes under bipolar pulses.
0.40, implying that about 60% of the formed particle dissolved. However, as explained above, this is not due to the inherent irreversibility of the electrochemical reactions but is a mechanical side effect determined by the loss of electrical contact between the tip and particle during particle shrinkage. As can be seen in Figure 6b, the normalized difference, that is, $(R_N - R_0)/R_N$, resembles the topography. This result also shows the point A well, which was not detected by the spatial map of $\Delta z$. Therefore, the normalized difference can be used to estimate the local reversibility of the silver redox process.

We proceeded to explore how humidity affects the reversibility of the silver redox process on the glass surface. Figure 7a–c shows topography images after the humidity-dependent bipolar FORC-IVz measurements using the same bias waveform shown in Figure 6b. Under these experimental parameters and up to 60% RH, we still observed crater-like topographic features in almost every position after the measurements, and the final $\Delta z$ values were nearly zero (Supporting Information, Figure S7). Thus, the fully reversible redox process occurred, at least in the central regions of the formed particles. However, at 90% RH, we did not observe the crater-like features and the final $\Delta z$ values did not return to zero, indicating that the electrochemistry becomes partially reversible. This differs from the loss of electrical/mechanical contact between the tip and the particle. Under high humidity conditions, the generated proton from water can participate in the conduction when applying a positive tip bias, leading to the incomplete dissolution process of the formed particles. We note that the reversibility of Ag redox processes is also affected by the number of cycles; that is, time. Time-dependent residual particle height shows that the $\Delta z$ returned to almost zero during the first two cycles but increased from the third cycle (Figure 7d). This can be explained by the increase in the probability of proton involvement in the Ag dissolution process over time.

In summary, we investigated the effect of humidity on nanoscale electrochemistry and its reversibility in a solid silver ion conductor using the FORC-IVz technique. Simultaneous detection of the local topographic height change of the sample and flowing current provides important information on the coupled and nonlocal cathodic and anodic processes, which is not available via separate measurements. Water did not play an important role in cathodic and anodic reactions at negative tip bias, but it was essential for processes at positive tip bias. The presence of water enables the anodic oxidation process at the tip–surface junction, leading to the continuous cathodic process at the bottom electrode; thus, steady-state Faradaic conduction is possible. In addition, the proton generated by oxidative water splitting played an important role in the ionic conduction as another mobile ionic species and mechanical softening of the glass, so the conductance enhanced and the depth of the hole decreased under high humidity conditions.

These findings illustrate the importance of humidity in nanoscale electrochemistry, memristors, atomic switches, ferroelectric switching, and similar devices, which is often overlooked. In particular, in SPM-based electrochemical research, probing, and devices the role of water is critical. Beyond functioning as a simple medium for charge transfer, water can control the entire electrochemical process, enhance the conductance and mechanical properties of the material, and affect the reversibility of redox processes. Finally, we want to highlight the dual nature of electrochemical SPM studies. SPM probes the local electrochemical processes occurring in nanoscale volumes beneath the tip, but this process significantly depends on the reaction at the counter interface separated spatially from the tip. Because either of the half reactions can be the limiting step of the total process, one should consider both even for very simple systems and control the counter reaction for the wanted reaction at the tip–surface junction. This study also revealed that the humidity-dependent FORC-IVz technique is a powerful tool for comprehensive understanding of nanoscale electrochemistry in ion conductors, memristors, and other electrochemical material systems.

ASSOCIATED CONTENT

Supporting Information

Additional details, Figures S1−S7, and Tables S1−S2. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: (S.M.Y.) yangs@ornl.gov.
*E-mail: (S.V.K.) sergei2@ornl.gov.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge J. M. Black for helpful discussion. This research was conducted at and partially supported by (E.S., A.T., and S.V.K.) the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Support (S.M.Y. and S.V.K.) was also provided by a DOE Presidential Early Career for Scientists and Engineers. This research was also partially supported (S.M.Y. and T.W.N.) by IBS-R009-D1, Korea. Materials synthesis work (M.P.P.) was sponsored by the Korea. Materials synthesis work (M.P.P.) was also partially supported (S.M.Y. and S.V.K.) was also provided by a DOE Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

REFERENCES
