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Additive manufacturing and characterization of AgI and AgI–Al₂O₃ composite electrolytes for resistive switching devices

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Brownlee, B. J., Tsui, L., Vempati, K., Plumley, J. B., Iverson, B. D., Peng, T. L., and Garzon, F. H., 2020, "Additive manufacturing and characterization of AgI and AgI – Al₂O₃ composite electrolytes for resistive switching devices," *Journal of Applied Physics*, 128, p. 035103. DOI: 10.1063/5.0004120

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Brownlee, Benjamin J.; Tsui, Lok-kun; Vempati, Karthik; Plumley, John B.; Iverson, Brian D.; Peng, Thomas L.; and Garzon, Fernando H., "Additive manufacturing and characterization of AgI and AgI–Al₂O₃ composite electrolytes for resistive switching devices" (2020). *Faculty Publications*. 5088.
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Cite as: J. Appl. Phys. **128**, 035103 (2020); <https://doi.org/10.1063/5.0004120>

Submitted: 07 February 2020 . Accepted: 03 July 2020 . Published Online: 17 July 2020

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Submitted: 7 February 2020 · Accepted: 3 July 2020 ·

Published Online: 17 July 2020

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ABSTRACT

This work investigates the electrochemical dynamics and performance of additively manufactured composite electrolytes for resistive switching. Devices are comprised of a Ag/AgI-Al₂O₃/Pt stack, where the solid state electrolyte is additively manufactured using extrusion techniques. AgI-Al₂O₃ composite electrolytes are characterized by x-ray diffraction and electrochemical impedance spectroscopy. The ionic conductivities of the electrolytes were measured for different concentrations of Al₂O₃, observing a maximum conductivity of 4.5 times the conductivity of pure AgI for composites with 20 mol. % Al₂O₃. There was little change in activation energy with the addition of Al₂O₃. Setting the Ag layer as the positive electrode and the Pt layer as the negative electrode, a high conductivity state was achieved by applying a voltage to electrochemically establish an electrically conducting Ag filament within the solid state AgI-Al₂O₃ electrolyte. The low conductivity state was restored by reversing this applied voltage to electrochemically etch the newly grown Ag filament. Pure AgI devices switch between specific electrical resistivity states that are separated by five orders of magnitude in electrical conductivity. Endurance tests find that the AgI resistive switches can transition between a low and high electrical conductivity state over 8500 times. Composite AgI-Al₂O₃ resistive switches formed initial Ag filaments significantly faster and also demonstrated two orders of magnitude separation in resistivity when cycling for 1600 cycles.

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I. INTRODUCTION

Ionic/electrochemical resistive switches have recently attracted attention as an alternative to traditional semiconductor devices as components in reconfigurable electronics,¹ next generation non-volatile memory (resistive random access memory),^{2,3} and neuromorphic computing,^{4,5} and antifusing.⁶ Advantages anticipated and demonstrated utilizing resistive switching include a greater potential for miniaturization, low power requirements, high speed transitions, high endurance, and radiation hardness.^{3,7,8}

Resistive switching behavior was first observed as early as the 1960s in oxides,⁹ and initial development of conductive bridging involving metal filaments for memory applications began at the end of the 1990s.¹⁰ Various methods have been employed to

achieve resistive switching such as electrochemical metallization, valence state change, and thermochemical systems.¹¹ One type of electrochemical resistive switching device consists of an active anode (such as Ag or Cu) and an inert cathode (such as Pt), with an electrically insulating, but ion conducting, solid state electrolyte positioned between the two electrodes.¹² By applying an electric field, a metal filament can be grown in the solid electrolyte by electroplating onto the active anode.¹³ This filament will continue to grow until it creates an electrically conductive path between the two electrodes (Fig. 1). In some systems, the metal filament is only stable under applied voltage and dissolves into the solid electrolyte in time once the applied voltage is discontinued, likely caused by migration of oxygen vacancies that lead to self-dissolution of the metal filament.¹⁴ In other systems, the grown filament is stable and

FIG. 1. Schematics of the (a) layers used to create electrochemical resistive switches and (b) cell after Ag filament formation. (c) Extrusion printed AgI (0% Al₂O₃) solid electrolyte (before burnout).

may persist until a reverse bias is applied that oxidizes the filament back into the solid state electrolyte.¹⁵ The setting and resetting between “ON” and “OFF” states allow for a reversible switching behavior between low and high resistive states.

Solid state electrolytes for this application have used oxides, chalcogenides, or halides and can be categorized into two types.^{11,16–18} In the case of solid state electrolytes such as SiO₂ without native Ag or Cu in the lattice, an initial reforming step is performed to load the electrolyte with the appropriate metal ion.¹¹ Silver halides including AgI, Ag₄KI, and Ag₄RbI have been extensively investigated as silver ion conducting materials.¹⁹ Silver halides are distinguished from solid electrolytes like SiO₂ because they contain mobile Ag⁺ ions without any ion loading step.²⁰ The transport mechanism for Ag⁺ in AgI is mediated by the Ag vacancies in the lattice.²¹ Higher ionic conductivity reduces the losses associated with ionic transport and could lead to faster switching devices. It has previously been shown in bulk material that when aluminum oxide (Al₂O₃) is added to AgI, the ionic conductivity can increase 100× compared to pure AgI due to space charge effects or the creation of a high conductivity interfacial phase.^{22,23} The influence of particle size and water absorption on the AgI conductivity enhancement has been evaluated, and it was observed that smaller particle sizes of Al₂O₃ yielded the largest improvements, up to a factor of 1000× with non-dried alumina.²⁴

The past studies were performed on bulk samples, and methods are sought for the fabrication of AgI composites in methods that are amenable to device fabrication. The integration of Al₂O₃ with AgI was demonstrated using porous alumina membranes^{25,26} and by high-pressure, high-temperature synthesis.²⁷ Additive manufacturing is a fabrication process that is promising for simplifying the deposition of composite materials and has recently been investigated for use in applications such as hierarchical ceramic devices.²⁸ Additive manufacturing has recently been demonstrated to be an effective means for the fabrication of printed electronics with techniques including inkjet, aerosol jet, and extrusion to print components.^{29,30} In extrusion-based additive manufacturing, the material of interest is loaded into a syringe and a multi-axis print platform controls the deposition of the material by applying a back pressure on the syringe while moving in a pattern designed by the user in computer-aided design (CAD) software. We have recently demonstrated the capability to deposit mixed-potential electrochemical sensors by extrusion of metal and perovskite electrodes onto ceramic substrates with an

yttria-stabilized zirconia (YSZ) electrolyte for exhaust gas emission sensing.³¹ The additive manufacturing technique is attractive because the deposition of AgI/Al₂O₃ composites by vapor deposition techniques is challenging due to the relatively low decomposition temperature of AgI and the high vaporization temperature of Al₂O₃. While the resolution of additive manufacturing cannot compete with microfabrication techniques such as photolithographic patterning, it enables the use of a wider variety of composite materials for printing discrete electronic components.

This work demonstrates the first use of additive manufacturing of AgI and composite AgI–Al₂O₃ electrolytes by extrusion printing for resistive switching applications in an Ag/AgI–Al₂O₃/Pt configuration. The transport properties of ionic devices are dependent on the film microstructure and while extensive characterization of AgI in pressed pellets and vapor deposited films have been previously reported,^{22,23} the ionic properties of AgI and AgI composites prepared by extrusion printing have not been reported until now. Deposited solid electrolytes were characterized by x-ray diffraction (XRD), microstructural analysis was performed by SEM, and electrochemical impedance spectroscopy (EIS) was used to study the influence of alumina loading on AgI’s ionic conductivity. The ionic conductivity was shown to increase when adding Al₂O₃ to AgI, with an observed 4.5 times increase in conductivity at 20% Al₂O₃. By applying opposite polarity voltages, an Ag filament was formed and then broken within the electrolyte. Optical microscopy with planar devices confirmed Ag filament formation within the additively manufactured electrolyte. Over five and two orders of magnitude in electrical conductivity were observed between the high and low resistive states for over 8500 cycles and 1000 cycles for the pure and composite electrolyte devices, respectively.

II. MATERIALS AND METHODS

A. Ink for composite AgI–Al₂O₃

AgI–Al₂O₃ ink for extrusion printing was prepared by overnight ball milling of solid AgI (Mallinckrodt) and different concentrations (0, 20, 40, and 60 mol. %) of Al₂O₃ (Almatis A16, 0.5 μm, α-phase) into a fine powder with 5 mm yttria-stabilized zirconia (YSZ) milling media in an ethanol dispersion. This powder was then dried overnight in an oven at 80 °C before being crushed and sieved through a #40 sieve (425 μm mesh size). The binder used for creating a paste was a 3.5:1 mass ratio of ESL ElectroScience 473 vehicle and 401 thinner. AgI and Al₂O₃ powders were integrated into this binder (65 wt. % AgI–Al₂O₃) using a Thinky ARV-310 centrifugal planetary mixer that mixed these components at 2000 rpm for 1 min. The pastes were then placed in a 5 ml syringe, centrifuged at 2500 rpm for 1 min, and degassed in the Thinky planetary mixer for 1 min at 2000 rpm under vacuum.

B. Resistive switch fabrication

Figure 1(a) shows the layers used to construct the electrochemical cells for resistive switching. Glass slide substrates were coated with 50 nm of Pt deposited by electron beam vapor deposition with a 5 nm adhesion layer of Ti. A Hyrel System 30M multi-material extrusion printer with a 0.41 mm nozzle (Nordson EFD SmoothFlow) was used to print AgI–Al₂O₃ on the Pt-coated glass

at a speed of 5 mm/s. The electrolyte was printed into 5 mm squares with an average thickness of 100 μm , as measured by profilometry. The printed electrolyte was dried in an oven at 120 $^{\circ}\text{C}$ for 20 min [see Fig. 1(c)]. The following heat treatment schedule was performed to de-bind the AgI– Al_2O_3 composite by vaporizing the organic binder:

- 1 $^{\circ}\text{C}/\text{min}$ to 100 $^{\circ}\text{C}$ with 2 h hold,
- 0.1 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$ with 2 h hold,
- 0.1 $^{\circ}\text{C}/\text{min}$ ramp to 325 $^{\circ}\text{C}$ with 2 h hold, and
- -3.0 $^{\circ}\text{C}/\text{min}$ ramp to room temperature.

A 5×5 mm² shadow mask was then used to deposit a 50 nm layer of Ag followed by a 50 nm layer of Pt capping layer onto the printed electrolyte using electron beam evaporation. Finally, a small amount of silver epoxy was manually placed on top of the Pt layer to reinforce the cell and prevent puncturing when attaching electrical leads. To visually track filament formation, a planar device was fabricated by printing AgI onto a glass slide and using a shadow mask to vapor deposit two 20 μm wide strips of Ag positioned 20 μm apart. Microscopy on these samples was performed with a Leitz Metalloplan optical microscope in transmission mode with the light source passing through a red-light filter to inhibit photo-reduction of AgI into Ag.

C. Characterization

X-ray diffraction (XRD) patterns were obtained of the composites with monochromatic Cu K-Alpha radiation on a Panalytical X-pert diffractometer. The measurement was taken in a standard θ/θ geometry with an X'Celerator detector. Slits used were as follows: incident Soller slit (0.04 rad), incident antiscatter slit (2°), incident divergence slit ($1/8^{\circ}$), diffracted beampath antiscatter slit (2°), and diffracted beam path Soller slits (0.04 rad). Analysis was performed with whole pattern fitting program JADE (Materials Data Inc.) with no additional data manipulation performed and fit to a quadratic background function. Reference diffraction data files from the ICDD PDF card database for Al_2O_3 and AgI were 01-070-5679 and 01-078-1614, respectively. Stylus profilometry was obtained using a Bruker Dektak system. Scanning electron microscopy was performed using a Hitachi S-5200 Nano SEM equipped with an Oxford Aztec X-MAX 80 energy dispersive x-ray spectroscopy system.

Electrochemical impedance spectroscopy (EIS) was performed using a Gamry Reference 600+ potentiostat an AC perturbation of 50 mV and a frequency range of 5 MHz to 0.1 Hz. The perturbation was selected in a range where the impedance response was linear so that the EIS assumptions of a linear response would be valid. Cables from the Gamry Reference 600+ were connected to clips that pressed onto the device samples. The impedance spectra were fitted to an equivalent circuit model using the Gamry Echem Analyst software. Impedance spectra were also obtained at 20 $^{\circ}\text{C}$ increments between room temperature and 150 $^{\circ}\text{C}$. For high temperature measurements, an Ni wire was fed through alumina tubes that were screwed into the clips.

D. Filament formation and switching

Filament formation and switching experiments were performed using a Keysight B1500A Semiconductor Device Analyzer.

With the Pt/AgI– Al_2O_3 /Ag cell, the Pt electrode on glass was grounded and the bias (positive or negative) was applied to the Ag electrode. Ag filaments (see Fig. 1(b)) were formed by electroreduction of Ag^+ onto the Pt cathode. The sources of electroplated Ag are mobile Ag^+ ions within the solid state electrolyte generated from the dissolution of Ag in the anode [Eqs. (1) and (3)]. At larger applied potentials, the Ag can also result from the reductive decomposition of the AgI electrolyte itself [Eq. (2)].³² Each reduction reaction was coupled with a concurrently occurring oxidative dissolution of Ag [Eq. (3)] or iodide oxidation to iodine [Eq. (4)] at the anode. The coupled Ag^+ reactions [Eqs. (1) and (3)] have a thermodynamic potential difference of zero since they are the same reaction written reversibly, though in reality, the overpotentials associated with charge transfer, nucleation, and diffusion make the onset voltage non-zero,

During the initial filament formation, a constant +7 V potential was applied to the cell until a significant change in current was observed. After the initial formation, the cell could then be easily transitioned back and forth between a high resistance state and a low resistance state. For pure AgI devices, the filament was broken by applying -3.5 V for 2 s and then reformed by applying 5 mA (about 0.6 V) for 0.5 s. For the composite AgI– Al_2O_3 devices, a higher breaking voltage of -7 V for 2 s and a higher reformation current of 30 mA for 0.5 s were needed to enable successful switching behavior. The initial filament was formed under a constant potential because of the high ionic resistance of the cell. As the filament grows, the distance between the anode and cathode shrink and the ionic resistance decreases. Once contact is made, a constant current was used to re-form the filament and was shown to reduce variability in the low resistance state. A constant current was chosen over a constant potential since the former allows us to directly control the growth rate. After forming or breaking a filament, the resistance was calculated from Ohm's law by applying a fixed voltage (-0.05 V) and measuring the induced current (averaged over 2.5 s). The small voltage was selected to not perturb the conductivity of the cell. For the high resistance state of pure AgI devices, it was found that the resistance was more consistently measured by applying a constant current of -100 nA and measuring the voltage for 2.5 s.

III. RESULTS AND DISCUSSION

A. Microstructure

Scanning electron micrographs of the printed AgI material and the composites are presented in Fig. 2(a). The AgI material takes the form of a bulbous microstructure with particles on the

FIG. 2. (a) Scanning electron microscopy of the microstructure of printed AgI shows that it is composed of bulbous particles of 2–5 μm in size. (b) SEM imaging of the AgI + Al_2O_3 20 mol. % composite shows sub-micrometer Al_2O_3 particles embedded within the AgI matrix.

order of 2–4 μm with observable porosity between the particles, though there appears to be continuous paths between each particle. This will extend the path length of conduction and increase the conductivity compared to a dense film. Small particles decorate the surface of the large bulbous structures but are artifacts of the electron beam induced reduction of AgI to Ag. We should note that this effect also exaggerates the porosity observed. The composite of AgI and Al_2O_3 at a 20 mol. % loading is shown in Fig. 2(b) and contains faceted particles between 0.5 and 1 μm randomly embedded within the AgI matrix. The particle size of the alumina particles is consistent with the manufacturer specified particle size distribution of Almatix A16. Energy dispersive spectroscopy (EDS) mapping (Fig. S1 in the [supplementary material](#)) confirmed the composition of the particles embedded in the AgI matrix.

B. XRD characterization

XRD patterns for AgI– Al_2O_3 composites are shown in Fig. 3, for 0%, 20%, and 40% Al_2O_3 . Peaks marked with A (black) are

FIG. 3. XRD patterns for AgI– Al_2O_3 composites for 0%, 20%, and 40% Al_2O_3 . Peaks marked with A are associated with $\alpha\text{-Al}_2\text{O}_3$ and peaks marked with B are from AgI. Solid lines indicate the measured data and the dashed lines indicate the whole pattern fitting from JADE.

associated with $\alpha\text{-Al}_2\text{O}_3$ and peaks marked with B (red) are associated with AgI. Peaks corresponding to $\alpha\text{-Al}_2\text{O}_3$ are clearly visible in the 20% $\alpha\text{-Al}_2\text{O}_3$ composite, and the peaks become larger in the 40% $\alpha\text{-Al}_2\text{O}_3$ composite. The diffraction data indicate that the deposited films are two-phase composites.

C. Ionic conductivity

Figure 4(a) shows Nyquist plots of AgI– Al_2O_3 composites for 0, 20, 40, and 60 mol. % Al_2O_3 taken at room temperature with an AC perturbation of 50 mV from 5 MHz to 0.1 Hz. The first semi-circle intercepts the horizontal axis at a frequency of 1 KHz and trends toward a large semicircle at low frequencies up to 0.1 Hz. The impedance measurements were fit to the equivalent circuit shown in the inset of Fig. 4(a), consisting of resistors (R_s) and constant phase elements (CPEs). R_1 represents the Ohmic resistance at the high frequency intercept, the R_2/CPE_2 pair represents the ionic conductivity associated with the first depressed semi-circle, and the R_3/CPE_3 pair represents the reactions impedance at the interface at the low frequency partial arc. The constant phase elements represent the capacitance associated with the bulk of the electrolyte (CPE_2) and the interfacial capacitance (CPE_3). R/CPE for the low frequency response was chosen in place of a Warburg term since there was clear curvature in the responses and the Warburg response is expected to be linear. Ionic conductivities obtained from the EIS data are plotted for the different Al_2O_3 composites in Fig. 4(b), with error bars representing the standard deviation from four samples. The ionic conductivity was calculated based on the geometric area of the cell (5 mm $\times$ 5 mm $\times$ 100 μm). At 20 mol. % Al_2O_3 , the ionic conductivity is 4.5 times the conductivity of pure AgI. This closely agrees with a maximum conductivity of 30 mol. % Al_2O_3 observed by others.³¹ The gains in conductivity are small compared with the results of Shahi and Wagner²⁴ and Uvarov *et al.*³³ showing over 3 orders of magnitude enhancement. In these works, smaller particle sizes (~ 60 nm) of alumina were used, and the pressing of the test pellets at high pressure would result in better densification compared with the AM technique. To improve on these results reported here, the logical next steps are to reduce the Al_2O_3 particle size to nanoparticles, the use of the gamma phase alumina,³³ and increasing the solids loading of the printed paste to decrease porosity.

FIG. 4. (a) Nyquist plots of AgI- Al_2O_3 composites for 0, 20, 40, and 60 mol. % Al_2O_3 at room temperature. Inset: Equivalent circuit used to model system. (b) Ionic conductivity normalized to cell geometry extracted from the EIS data in (a) as a function of Al_2O_3 concentration, with error bars representing the standard deviation from four samples.

FIG. 5. Ionic conductivity as a function of temperature for pure AgI and AgI with 20% and 40% Al_2O_3 .

D. Activation energy

The influence of temperature on the ionic conductivity of the composite electrolytes was determined by taking EIS measurements every 20 °C from room temperature up to 140 °C, close to the phase transition temperature of AgI. The conductivity data are plotted in Fig. 5 for pure AgI and AgI with 20 and 40% Al_2O_3 . Conductivity for each composition followed an Arrhenius relationship, and activation energies were determined to be 0.55, 0.61, and 0.59 eV for 0%, 20%, and 40% Al_2O_3 , respectively. These activation energies are similar to that from Lee *et al.*, who reported activation energies from 0.285 to 0.472 eV for polycrystalline AgI and 0.7 eV for single crystal AgI (C-axis).²¹ A higher activation energy is observed compared with the composite samples produced by Lee *et al.*, as well as lower conductivities compared to the pellet samples they investigated.²¹ Additionally, an upward curve near the phase transition region was not observed. This is likely to be due to grain boundary resistance at the interface between printed particles as the dominant factor in slowing down ion transport and suggests that improving the ionic conductivity would be achieved by either reducing porosity and the number of grain boundaries. For the construction of devices, these results also point to the need to reduce the thickness of the printed structures.

FIG. 6. (a) Current with time during the initial Ag filament formation through $\sim 105\ \mu\text{m}$ thick AgI and AgI- Al_2O_3 (20 mol. % Al_2O_3) electrolytes between Pt and Ag electrodes with an applied +7 V. (b) Time for initial Ag filament formation in pure AgI as a function of AgI thickness.

E. Filament formation

Successful initial filament formation in stacked devices (see Fig. 1) was evident by nearly 3 orders of magnitude increase in measured current up to the limiting current of the sourcemeter seen in Fig. 6(a). The average current through the pure AgI was $30\text{ }\mu\text{A}$ during filament formation, and the average current through the AgI- Al_2O_3 electrolyte was nearly double at $56\text{ }\mu\text{A}$. The limiting current of the AgI device was set to 10 mA, but a better filament connection in AgI- Al_2O_3 was observed when the limiting current was set to 20 mA. The filament in the pure AgI device in Fig. 6(a) short circuited the electrodes in 840 s, while the AgI- Al_2O_3 composite with 20% Al_2O_3 shorted in only 84 s. Thus, the higher ionic conductivity of the composite electrolyte leads to higher current during filament formation resulting in quicker formation times.

The initial formation time was found to be correlated with the electrolyte thickness. Figure 6(b) shows a linear relationship between AgI thickness and initial formation time. It should be noted that the initial formation of the filament takes significantly longer than subsequent cycles, typically taking hundreds or thousands of seconds to form; once the initial filament formation has taken place, subsequent re-formations take less than 0.5 s. This suggests that the entire filament is not completely broken when a negative potential is applied and that only the interface between the filament and the electrode is disrupted, as observed by others.³⁴

F. Optical imaging of filaments

Ag filament formation in AgI was confirmed by optical microscopy images of a planar device, consisting of two Ag electrodes deposited on AgI. Two Ag electrodes, as opposed to one Ag and one Pt, were used for fabrication simplicity. Although the planar device likely produces different filaments than the stacked device due to the different geometry and composition, it is still instructive to see the filament in the AgI electrolyte. Figure 7(a) shows the initial state of the device before applying a potential. Applying +7 V to this device induced filament growth, which shorted the electrodes in ~ 75 s. This connection can be seen in Fig. 7(b), visually confirming Ag filament formation. Microscopy on the planar devices also confirmed that the filament becomes thicker if the positive potential is sustained for longer times and that it is possible to have multiple filaments for a single device (see Fig. S1 in the supplementary material). This variability in the

filament structure can explain the variation in electrical conductivity when different voltages are applied. It should be noted that concentrating the current by using triangular tipped electrodes instead of rectangular electrodes could improve repeatability and reduce the formation potential.³⁵ Once transitioned to a low resistance state, it is impossible to transition the planar device back to a high resistance state since reversing the applied voltage to etch the established Ag filament extending from one Ag electrode simultaneously grows a new Ag filament extending from the other Ag electrode. However, while an Ag/AgI/Ag device is not viable for switching applications, it does show promise for use as an antifuse, which creates a permanent electrical connection after a threshold voltage is exceeded.

G. Switching behavior

Unlike the planar device, the inert Pt electrode in the stacked electrochemical switch enables filament breaking under a negative potential by limiting the extent to which an Ag filament can grow on the Ag electrode to the amount of silver that was electroplated onto the Pt. This allows the electrochemical switch to return to a high resistance state similar to that before filament formation. A plot of repeated transitions between a high and low resistance state for a pure AgI device is shown in Fig. 8(a) indicating stable resistivity for these states over many cycles. Figure 8(b) shows the distribution of high and low resistivities for a pure AgI device over 8500 cycles, with nearly 5 orders of magnitude in the peak-to-peak separation. Two orders of magnitude separate the majority of the values, with 98.15% of high resistance values above $10^6\text{ }\Omega\text{ cm}$ and 99.45% of low resistance values below $10^4\text{ }\Omega\text{ cm}$. These resistance ranges were comparable for three separate devices. Figure 8(c) shows the switching behavior for a composite AgI- Al_2O_3 (20% Al_2O_3) device for 1600 cycles. The composite switch failed shortly after 1600 cycles by staying continuously in the low resistance state. Careful optimization of the composite microstructure and switching voltages may allow higher switching numbers. The distribution of resistivities for AgI- Al_2O_3 cycling is shown in Fig. 8(d), showing a lower separation in the high and low resistive states than pure AgI. Despite this lower separation, there was still a two order of magnitude peak-to-peak separation and one order of magnitude separation for the majority of the values, with 99.25% of high resistance values above $2 \times 10^4\text{ }\Omega\text{ cm}$ and 99.66% of low resistance values below $2 \times 10^3\text{ }\Omega\text{ cm}$.

FIG. 7. Optical microscope (transmission mode) images of filament growth on a planar device. (a) Two Ag electrodes (black) deposited on pure AgI (red, with color from a red filter). (b) Ag filament formation, indicated with an arrow, after a +7 V potential for 75 s.

FIG. 8. (a) Measured high and low resistivities for a pure AgI device for 8500 cycles and (b) distribution of resistivity data for the AgI device. (c) Measured high and low resistivities for a composite AgI- Al_2O_3 device with 20% Al_2O_3 for 1600 cycles and (d) distribution of resistivity data for the AgI- Al_2O_3 device.

IV. CONCLUSIONS

Solid state AgI and AgI- Al_2O_3 composite electrolytes were successfully made by extrusion printing, additive manufacturing techniques. The electrolytes were characterized by x-ray diffraction and electrochemical impedance spectroscopy. The ionic conductivity was shown to increase when adding Al_2O_3 to AgI, with an observed 4.5 times increase in conductivity at 20 mol. % Al_2O_3 . The electrolytes were used in electrochemical resistive switches, where a Ag filament was formed and broken within the electrolyte. Ag filament formation within the electrolytes was observed by optical microscopy. The pure AgI resistive switches demonstrated nearly five orders of magnitude difference in electrical conductivity between the high and low resistive states for over 8500 cycles. Composite AgI- Al_2O_3 resistive switches formed initial Ag filaments in significantly less time and also demonstrated two orders of magnitude separation in resistivity when cycling for 1600 cycles. Both pure AgI and AgI- Al_2O_3 composites were shown to be effective solid electrolytes. Additive manufacturing of solid electrolytes overcomes challenges in fabrication associated with other techniques of creating composite electrolytes and enables the use of a wider variety of composite materials. This suggests that additive manufacturing is a potentially advantageous route to make electrochemical resistive switches and for printing discrete electronic components.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for energy dispersive spectroscopy (EDS) mapping measurements and optical microscopy of filament growth under high applied potential.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the Air Force Research Laboratory and the Utah State University Space Dynamics Laboratory. The work of Benjamin J. Brownlee and Karthik Vempati was supported by the Air Force Research Laboratory Summer Scholars Program. This material was assigned a clearance of CLEARED on 19 November 2019. Case Number: AFMC-2019-0713. The authors acknowledge the support from Sandia National Laboratories for access to the tools to synthesize the pastes and print the devices described here. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government. SAND2018-14094J.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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