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# Fabrication of Microconfigured Multicomponent Ceramics

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**Microfabrication by coextrusion is a novel ceramic processing technique capable of creating complex ceramic–metal structures. These structures are fabricated by multiple pass coextrusion of a feedrod comprised of several powder-filled thermoplastic compounds. The compounds contain either ceramic, metal, or fugitive powders. To illustrate the capabilities of microfabrication, a demonstration part containing lead manganese niobate–lead titanate ceramic and silver palladium was fabricated. The final part was microconfigured, with a fenestrated structure containing 3110 repeat units per square centimeter. The repeat unit feature sizes were 15 and 5 μm for the ceramic and electrode, respectively. Microfabrication by coextrusion is proposed as a fabrication technique for the production of smart structures and materials.**

## I. Introduction

The linear strains produced by piezoelectric and electrostrictive ceramics are typically less than 0.1% in polycrystalline ceramics, up to approximately 1% for recent single crystals.[1] To compensate for this, researchers in the field of ceramic actuators have turned to strain-amplifying architectures. Strain amplification can be accomplished in one of two ways. The first is the use of a monolithic stack, much like a multilayer capacitor, connected to a system of levers. The net displacement of the individual layers is amplified by external leveraging.[2] The second design utilizes internal leveraging. The internally leveraged ceramic actuator shown in Fig. 1 is a simple bimorph bender. It is driven by a field-induced strain mismatch between the two active ceramic layers.

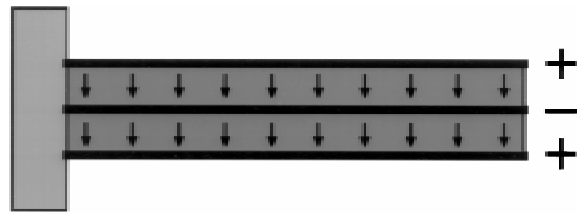


**Fig. 1.** Internally leveraged simple bimorph bender.

The tip deflection of bender actuators can be exploited to create high-performance actuators.[3] The miniaturization of actuators and their combination into series and parallel arrays has the potential to improve performance by at least 1 order of magnitude.[4] The arrangement of individual actuators into series and parallel arrays maximizes both force and net deflection (strain), as depicted in Fig. 2. Miniaturization will allow the benefits of arrays in a physically compact package. The term ‘‘microconfigured’’ can be applied to materials containing complex microscopic architectures. Some possible applications include active vibration damping, microvalving, advanced surgical tools, and surface morphology control. Discussion of the trade-offs involved with the individual actuator designs is the topic of much debate in the smart materials and structures literature and therefore will not be discussed here.

The realization of microconfigured materials will require a processing technique that is capable of meeting two key requirements: the fabrication of complex microscopic electrode and ceramic forms, and the generation of released forms that contain engineered empty space to allow the independent motion of each actuator in an assembly. Several ceramic processing techniques exist that are capable of fabricating miniature ceramic parts. However, it is impractical to use any one of them to fabricate electroded ceramic with the complexity required by microconfigured ceramic actuators. Tape casting is capable of making monolithic structures containing several ceramic and electrode materials, but the final part is small in only one dimension. Objects produced via LIGA (lithography, electroforming, and molding) have very fine features, but their aspect ratio is limited.[6] Micromilling, a material removal method, is limited by the size of the tooling and the cutting stresses involved.[7] Rapid prototyping (RP) technologies are currently emerging as leaders in three-dimensional part production; however, each RP method is limited by the primitive feature dimensions of the build technique.[8] The complexity of an injection-molded ceramic part is limited by the mold, and by the precision of postfiring electroding procedures. Microfabrication by coextrusion (MFCX) is a novel processing technique capable of creating arrays of microsized ceramic and electrode objects with individual feature sizes on the order of several micrometers. The ratio between part dimensions in the *x*–*y* to *z* directions, or aspect ratio, is unlimited. The ability of MFCX to create complex ceramic shapes has been demonstrated in previous research efforts.[9–11]

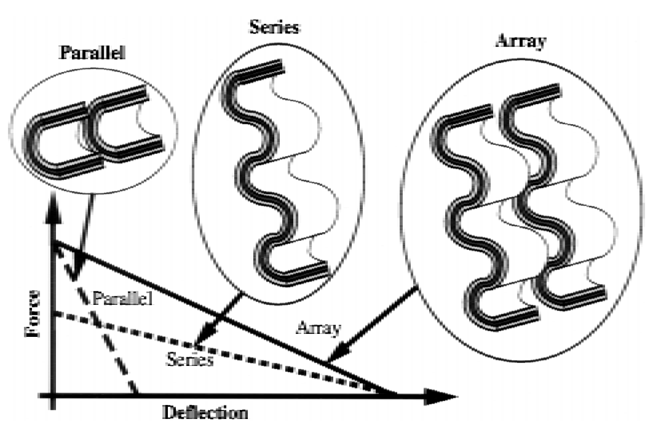


**Fig. 2.** Enhancement in the force-deflection performance of bender actuators realized by combining arrays of benders in series and parallel. (After Moskalik and Brei.[5])

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**Table I. Brabender Torque Rheometer Results at 140°C**

| Compound | Solids loading (vol%) | Apparent melt viscosity (Pa·s) | Apparent shear rate ($s^{-1}$) |
|---|---|---|---|
| Ceramic | 56 | 1520 | 222 |
| Electrode | 54 | 1610 | 222 |
| Fugitive | 47 | 1650 | 222 |

The MFCX process was used to create a demonstration part to illustrate the capability of MFCX to fabricate microconfigured multicomponent materials. The demonstration part contains fenestrated structures of microsized lead manganese niobate–lead titanate (PMN–PT) ceramic and silver palladium electrode. These complex metal–ceramic objects were fabricated coincidentally, alleviating the need for postprocessing electroding procedures. The cofired part is a stand-alone macroscopic device containing thousands of individual repeat units.

## II. Experimental Procedure

An electrically heated high-intensity shear mixer[†] was employed to create an extrudable compound of powder and thermoplastic. Ethylene ethyl acrylate[‡] and acryloid[§] resins were melted at 140°C in the mixer. The desired amount of powder (PMN–PT,[¶] AgPd,[††] or Carbon Black[‡‡]) was combined with the melt. Heavy mineral oil[§§] was added as a processing aid to ensure a consistent apparent melt viscosity value. Three separate compositions were prepared: a PMN–PT ceramic compound, a silver palladium electrode compound, and a carbon black fugitive compound. The solids loading values, apparent melt viscosities, and apparent shear rates are listed in Table I.

The different compounds were compression molded at 100°C into sheets of varying thickness using stainless steel dies. The sheets were assembled as shown in Fig. 3 to create the repeat unit used in the demonstration part. The assembly of sheets was uniaxially pressed at 1 MPa and 120°C to create a multicomponent feedrod for extrusion.

The single-piece parallelepiped feedrod (25 mm × 25 mm × 100 mm) was extruded through a symmetric 6:1 square reduction die using a piston extruder.[¶¶] The material exiting the die, or extrudate, had a cross section identical to that of the feedrod, while its dimensions were reduced by a factor of 6. The cross-section shape retention and size reduction of the extrudate are depicted in Fig. 4.

Sections of the first extrudate were then bundled together with sheets of ceramic-filled compound to create 16-element assembly of interlinked repeat units. The individual pieces were uniaxially pressed at 1 MPa and 120°C to create the second feedrod as illustrated in Fig. 5. After the second extrusion, the initial repeat unit had undergone a total size reduction of 36 times. The 25 mm green repeat unit was reduced to 700 μm.

Thirty-six sections of extrudate from the second extrusion were cut to length, bundled, and uniaxially pressed to create the third feedrod. The third extrusion step resulted in a total size reduction of 216 times. Figure 6 shows the bundling scheme and extrusion step employed to create the final assembly. The final extrudate contained 3110 repeat units per square centimeter. Sections of green extrudate from the first, second, and third extrusion steps are shown in Fig. 7.

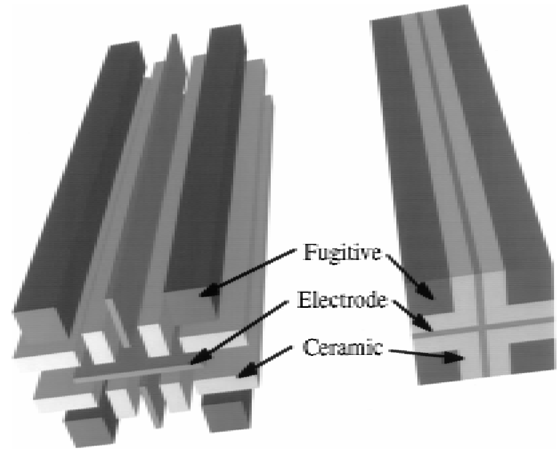


**Fig. 3.** Initial feedrod fabrication from warm-pressed sheets of powder-filled thermoplastic.

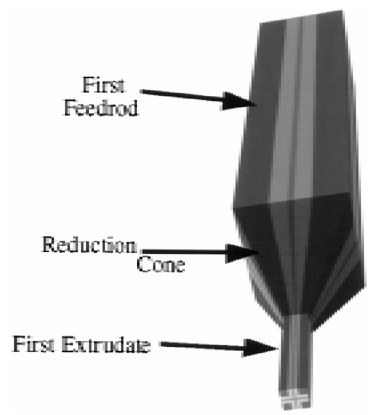


**Fig. 4.** First extrusion schematic depicting the shape retention and size reduction of the first feedrod.

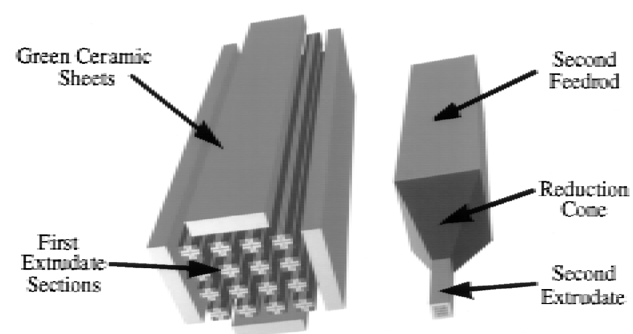


**Fig. 5.** Schematic depiction of the second feedrod formation and second extrusion step.

The third extrudate was cross-sectioned into pieces 2 mm tall and cofired in a two-stage process. the thermoplastic binder was removed during a 60 h binder burnout to 600°C in flowing air (Table II). The binder removal heating schedule was devised from thermogravimetric analysis (TGA)[†††] of the three extrusion compounds. Once binder burnout was completed, the parts were sealed in an alumina crucible along with 1 g of a sacrificial lead oxide–alumina setter powder, 90 wt% alumina–

[†]Plasti-Corder PL 2100 Electronic Torque Rheometer, C. W. Brabender, South Hackensack, NJ.
[‡]EEA 6182, Union Carbide, Danbury, CT.
[§]Acryloid B67, Rohm and Haas, Philadelphia, PA.
[¶]PMN–PT, 90% $Pb(Mg_{1/3},Nb_{2/3})O_3$–10% $PbTiO_3$, AVX, Myrtle Beach, SC.
[††]PGP 7071, PGP Industries Inc., Santa Fe Springs, CA.
[‡‡]Cabot Black Pearls BP-120, Cabot Corp., Boston, MA.
[§§]Heavy Mineral Oil, Witco, Petrolia, PA.
[¶¶]Bradford Small Scale Extrusion Unit, Bradford University Research, Ltd., West Yorkshire, U.K.
[†††]TGA Model TG-171, Cahn Instruments Inc., Cerritos, CA.

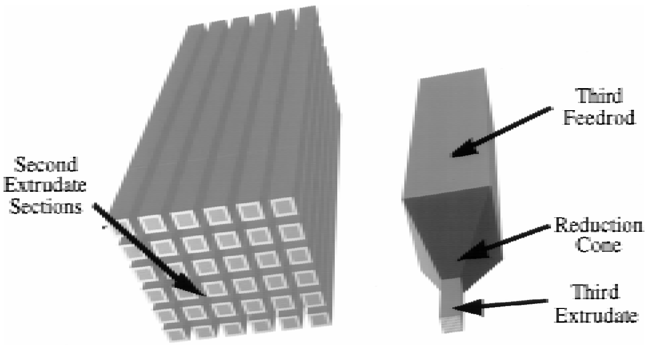


**Fig. 6.** Schematic depiction of the third feedrod formation and final extrusion step.

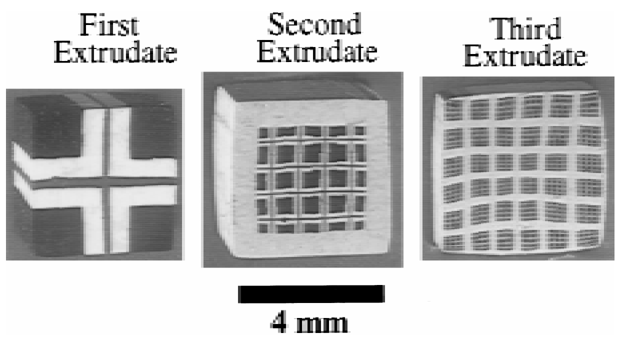


**Fig. 7.** Sections of green extrudate from the first, second, and third extrusion steps.

**Table II. Thermoplastic Binder Removal Schedule**

| Ramp rate (°C/h) | Temperature (°C) | Hold time (h) |
|---|---|---|
| 120 | 210 | 0.5 |
| 3 | 300 | 0 |
| 4 | 350 | 0 |
| 5 | 400 | 0 |
| 15 | 450 | 1 |
| 300 | 600 | 0 |

10 wt% PbO. The parts were sintered to full density in a lead-rich atmosphere by heating the sealed crucible at 10°C/min to 1050°C and holding for 0.5 h in flowing air. The fully dense parts were furnace cooled. A section of cofired extrudate was mounted in epoxy and diamond polished for energy dispersive spectroscopy[‡‡‡] (EDS) analysis.

## III. Results and Discussion

### (1) Forming Process

The rheological difficulties associated with the coextrusion of two or more thermoplastic compounds are overcome by practitioners in the polymer industries through the use of complex multiple manifold coextrusion dies.[12] The dimensions and complexity of the coextrusion die dictate the minimum feature sizes achievable. To avoid this constraint, the MFCX process utilizes a fugitive material that allows fabrication of any two-dimensional shape using a simple square cross-section die. The fugitive material is not only designed to act as a space-filling buffer between the ceramic and electrode shapes and the die wall, but also to be oxidized during cofiring. The volume left

‡‡‡SEM Model S3200N, Hitachi.

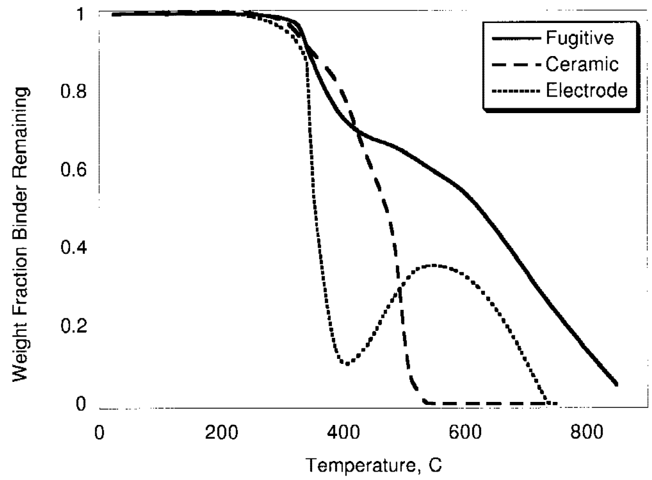


**Fig. 8.** Thermogravimetric analysis results from the ceramic, electrode, and fugitive extrusion compounds.

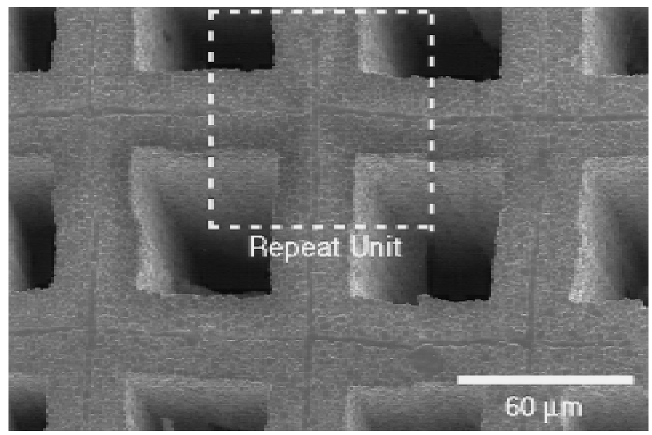


**Fig. 9.** SEM micrograph showing the microconfigured structure of the final part. The repeat unit highlighted in the micrograph has undergone size reduction from 25 mm to 60 μm in three extrusion steps.

vacant by the removal of the fugitive material creates empty channels in the fenestrated demonstration part shown here. For future microfabricated actuators, it creates released forms that allow freedom of motion between individual repeat units.[13]

The MFCX process utilizes a multicomponent feedrod system. As described in the experimental section, the feedrod contains an arbitrary number and arrangement of extrusion compounds containing either ceramic, metal, or fugitive powder. Similar rheological behavior among the various green body components is critical for shape retention during coextrusion. A mismatch between the viscosities of the various compounds will result in encapsulation of the higher-viscosity material by the lower.[14] The high shear mixer is used as a torque rheometer during compounding to match the rheological behavior between the different extrusion compounds.[15]

### (2) Binder Removal and Sintering

The transition from green body to sintered object requires careful cofiring management. The first stage, room temperature to 600°C, involves pyrolysis of the thermoplastic resin and oxidation of the carbon black fugitive. The pyrolysis behavior of all three compounds was examined via thermogravimetric analysis, the results of which are shown in Fig. 8. During pyrolysis, silver palladium catalyzes the degradation of the polymer binders by an organometallic reaction.[16] The binder burnout schedule compensates for the wide distribution in initial weight loss temperatures observed in the three compounds. This reduces the possibility of flaws at the interface between

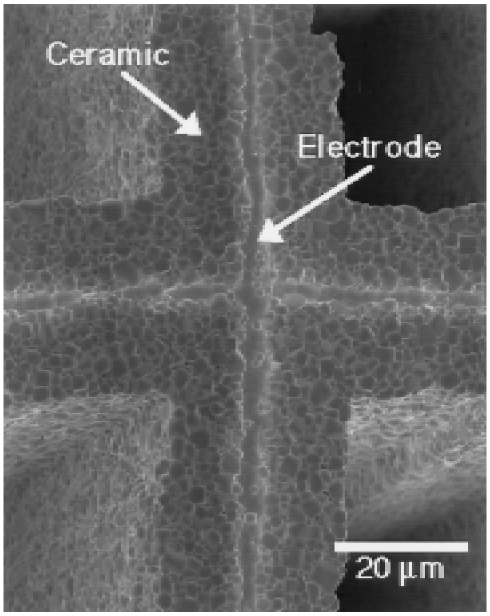


**Fig. 10.** SEM micrograph showing the PMN–PT ceramic and AgPd electrode within the repeat unit.

the two dissimilar materials caused by a mismatch between the rates of gaseous by product evolution and bulk diffusion through the surrounding material.[17] The second stage, 600° to 1050°C, requires a balance between the kinetics of oxidation and reduction of palladium. In an oxidizing atmosphere, palladium forms an oxide between 450° and 650°C. The difficulties associated with this are twofold: the oxide occupies 1.68 times the original volume of palladium, and the evolution of oxygen above 650°C may form gas bubbles in the electrode layers.[18] Oxidation of the electrode is kinetically limited by rapidly heating through the temperature regime where the oxide is stable. Above the stability temperature, the risk of oxygen bubble formation is minimized by slowing the heating rate and hence densification. The gaseous oxygen diffuses rapidly through the porous metallic matrix. Superimposed upon the behavior of the electrode materials is the requirement of complete carbon oxidation. It is imperative that any residual carbon be oxidized below 750°C to avoid a carbothermic reaction with the PMN–PT ceramic.

The addition of a small volume fraction of ceramic powder to the silver palladium compound aids in the successful cofiring of these parts. The ceramic grog acts both as a sacrificial lead source, to compensate for the solubility of lead in silver palladium, and as an alternate path for the diffusion of silver into the ceramic.[19–22] The ceramic particles were also observed to reduce the likelihood of delamination flaws at the interface between ceramic and electrode; it is believed this is due to an improvement in the mechanical adhesion at the interface.[23,24]

### *(3) Microconfigured Structure*

A cofired fenestrated demonstration part was created to illustrate the ability of MFCX to fabricate arrays of microsized electroded ceramic structures. Figure 9 is an SEM micrograph showing six of the 16 repeat units contained in one of the 36 modular assemblies of the third extrudate. The highlighted portion of the micrograph delineates the repeat unit contained in the first extrusion feedrod. The original unit, containing ceramic, metal, and fugitive compounds, has undergone three extrusion steps to enact an overall size reduction of 216 times. The individual repeat units exhibit excellent shape retention and consistent electrical registration between neighbors. The

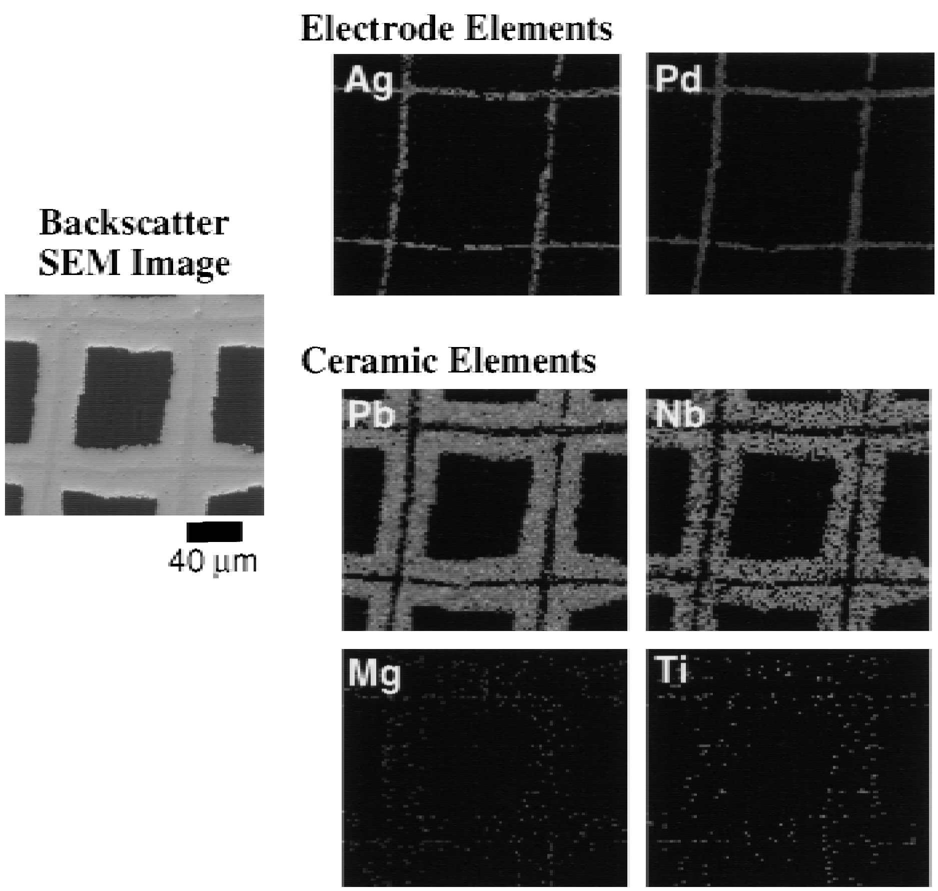


**Fig. 11.** Backscatter SEM micrograph of the representative area used for EDS. Individual elemental maps of the ceramic and electrode constituents.

depth of field available in the SEM serves to illustrate both the regions made vacant by oxidation of the fugitive and the large aspect ratios available with MFCX. Figure 10 highlights the 5 μm silver palladium electrode running through the center of each repeat unit. These micrographs display the ability of MFCX to produce parts with a high degree of two-dimensional complexity coupled with a highly variable third dimension.

A backscatter mode micrograph of the representative area is shown in Fig. 11 along with the individual elemental maps obtained by EDS. The configuration of the ceramic fenestrations is clearly shown by the location of the lead, manganese, niobium, and titanium elements that comprise the PMN–PT ceramic. The location of the elements in the silver palladium electrode and their connectivity is evidenced by their uninterrupted elemental scan. X-ray analysis confirmed the phase purity of the cofired PMN–PT ceramic.

The structure highlighted in this article was fabricated to demonstrate the capabilities of MFCX to create multicomponent structures with the complexity required to realize arrays of microactuators. Two actuator design points were not included in the fenestrated structure; unconstrained motion and lead attachment. Both of these issues can be addressed with the addition of a series of contact pads.[25] At each bundling stage of the extrusion process, large contact pads containing ceramic and electrode are added to the perimeter of the feedrod. During coextrusion and subsequent bundling steps, these contact pads ensure accurate registration between neighboring assemblies. Careful design of the contact pads and coextrusion scheme ensures no extraneous material is added that would constrain the net displacement behavior of the final actuator array. The final part would contain an array of miniaturized actuators linked together in an outwardly expanding manner similar to the layout of a printed circuit board. As a result, a microsized array can be driven with the use of two or three electrical leads (the exact number of leads depends upon the actuator design). The complexities usually associated with lead attachment and net displacement constraints can be circumvented with this technique.

## IV. Conclusions

Microfabrication by coextrusion was shown to be a viable technique for the fabrication of complex microsized structures of ceramic and metal. Fenestrated PMN–PT–silver palladium structures containing 3110 individual repeat units per square centimeter were successfully fabricated and cofired. These structures were released forms demonstrating excellent shape retention and electrode connectivity. The fully dense parts were comprised of 5 μm silver palladium electrodes with 15 μm PMN–PT ceramic walls. The MFCX technique is capable of fabricating densely packed two-dimensional arrays of fully electroded ceramic objects with highly complex layouts.

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