Design of Ordered Nanoporous Metals though Two Photon Polymerization

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3. Abstract

Recently developed mechanical actuators based on nanoporous metals have shown similar properties to traditional piezoelectric ceramics while requiring voltages up to two orders of magnitude smaller [1]. The current synthesis techniques of nanoporous metals result in a disordered structure. In a nanoporous metal the macroscopic properties are the result of the interactions between individual subunits. Therefore, control over the nanostructure will allow for control over these interactions and ultimately the macroscopic properties. The actuating properties of the nanoporous metals is a result of surface phenomena so it is important that the pore size of any structure created is less than 200nm to ensure enough surface area. This project proposes a process to create ordered nanoporous metals using a two photon polymerization technique for use as mechanical actuators with superior properties to traditional piezoelectric ceramics. In addition, this project will also work in incorporate a solid electrolyte into the processing of the nanoporous metal.

4. Duration of Project

The project will last four years, since this will be the applicant's time as a PhD student.

5. Personnel

The personnel working on this project are all part of the Material Science group at the Zernike Institute for Advanced Materials.

Prof. Dr. J.T.M. De Hosson (professor/ group leader of Material Science Group)

Brian Smith (Applicant/ PhD Student)

Ing. P. van den Dool (Technician)

6. Cost Estimates (in k€)

		2010	2011	2012	2013	Total
Position	PhD Students Postdocs Technician Guests	1 – – –	1 – – –	1 – – –	1 – – –	
Cost	Personnel Running Budget Equipment	43 10 100	43 10 0	43 10 0	43 10 0	172 40 100
	Total	153	53	53	53	312

7. Research Program

7.1. Introduction

Mechanical actuators are of vital importance for many technological applications. Materials suitable for use as actuators must be able to reversible change their shape in response to an external stimulus, the most common being an applied voltage. Currently piezoelectric ceramics are the material of choice for applications of actuators. However, recently several other materials for use as mechanical actuators have been studied such as polymers, carbon nanotubes, and nanoporous metals [2].

In nanoporous metals the introduction of surface charges though an applied voltage will result in the formation of a narrow space charge layer on the surface of the metal. This process is analogous to the formation of space charge in MOSFETs to alter the conduction of the semiconductor. In semiconductors the width of the space charge region can range from 10 to 1000 lattice constants [3]. For metals the space charge region will be much narrower because the high density of conduction electrons serves as an efficient screening mechanism [1]. As a result, the induced charge remains localized very close to the surface where it will alter the local density of states in this region of the metal. The change in the density of states will cause a change in the atomic bonding potentials resulting in the formation of surfaces stresses. However, due to the extremely thin region in which the surface stresses will develop only structures with very high surface to volume ratios will be able to utilize this phenomenon for controllable properties.

Actuators based on nanoporous metals have several advantages over traditional piezoelectric ceramics. Nanoporous metals can achieve similar actuating properties at voltages up to two orders of magnitude smaller than piezoelectric ceramics. Nanoporous metals are also much more stable materials than ceramics which are brittle and have low cycle lifetimes [2].

Current nanoporous metals are synthesized using electro-chemical driven dealloying of a binary alloy [4] or by randomly compacted metal nanoparticles [1]. Both techniques result in a highly disordered nanoporous metal. The disorder of these materials prevents the effective transfer of localized surfaces stresses to the macroscopic scale. As a result the mechanical properties are severely degraded. Creating an ordered nanoporous metal will allow control over the transfer of the localized surface stresses through the material allowing superior actuating properties. Furthermore, control over the structure of a nanoporous metal will create another tunable parameter to control the actuating properties of these materials.

In this project we propose creating ordered nanoporous metals using a two photon polymerization process by femtosecond laser pulses. This technique has recently been used to create 3D metallic nanostructures but as of yet synthesis of nanoporous metals has not been attempted.

7.2. Two Photon Polymerization

Photopolymerization is a photochemical reaction that is widely used for laser processing of materials. In this process a polymer resin undergoes a liquid to solid phase change upon laser irradiation. This process has been used to fabricate sub-micron structures for many applications such as optical components and micromechanical devices [5].

During photopolymerization laser light is used as an energy source for the conversion of small liquid molecules into solid macro-molecules. Solidification can take place through two mechanism; crosslinking and polymerization. The difference between these two processes is highlighted by examining the quantum yield (ratio of number of polymerized units to number of photons absorbed) associated with each process. For crosslinking, chemical bonds that crosslink molecules are formed. Each crosslink requires the absorption of a photon so the quantum yield will be less than 1. Polymerization is a chain reaction by which monomers are added to an expanding polymer chain. In this process the absorption of a single photon sets off a chain reaction so the quantum yield will be much larger than 1 [5]. Because of the large quantum yield associated with photopolymerization this will be the dominate mechanism for the liquid to solid phase change. The polymerization process consists of three steps; photoinitiation, chain propagation, and termination.

During the first step a photointiator species absorbs a photon producing an active species which can be a radical or a cation (Equation 1). There are several chemical processes that will create active species such as double-bond addition of acrylates and ring-opening of expoxides [5]. The photoinitator is a small light weight molecule that is more sensitive to light than the monomers. Once an active species has been generated they will "attack" the monomers creating monomer radicals. These monomer radicals will then react with more monomers in a chain reaction (Equation 2). This reaction will stop when two radical monomers react with each other and can terminate in two ways (Equation 3a and 3b).

$$I \xrightarrow{h\nu} I^* \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + M \longrightarrow RM\cdot \xrightarrow{M} RMM\cdot \cdots \longrightarrow RM_n\cdot \qquad (2)$$

$$RM_n\cdot + RM_m\cdot \longrightarrow RM_{m+n}R \qquad (3a)$$

$$RM_n\cdot + RM_m\cdot \longrightarrow RM_n + RM_m \qquad (3b)$$

I=photoinitiator, R·=radical, M=monomer, M·=radical monomer [5]

Two photon absorption is a quantum mechanical process by which an electron absorbs two photons "simultaneously" to overcome an energy gap. This process is schematically shown in Figure 1 [5]. After the absorption of the first photon a virtual intermediate state is created which will have a very short lifetime (on the order of femtoseconds). If a second photon is absorbed before the decay of this virtual state then the electron will be able transcend the energy gap.

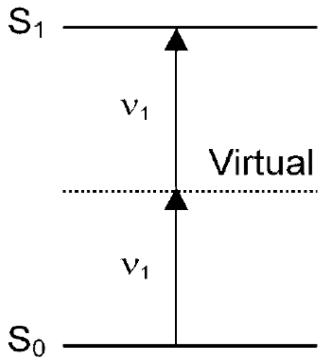

Fig 1. Schematic of two photon absorption process [5]

Two photon absorption can be utilized for photopolymerization. This process has a number of advantages over single photon polymerization. Instead of absorbing one high energy (ultraviolet) electron, polymerization can take place using two photons with longer wavelengths in the infrared (IR) region. The advantage of using IR is that most polymers have negligible absorption in this region of the spectrum [5]. As a result an IR laser will be able to photopolymerize regions inside the material while leaving the rest undisturbed. In two photon polymerization there is a quadratic dependence of the polymerization rate on the laser intensity allowing much greater spatial resolution than single photon-polymerization.

In two photon polymerization structures with dimensions smaller than the diffraction limit of the optical system can be created due to the nonlinear nature of the two photon polymerization process. For a given optical set-up the focal spot size of the laser will be diffraction limited. However, the two photon polymerization rate depends on the square of the light intensity. As a result, within the focal spot there will be a smaller volume in which the laser intensity exceeds the threshold value and two photon polymerization will occur, Figure 2 [5]. In this case the diffraction limit determines the size of the focal spot not the dimension of the polymerized volume.

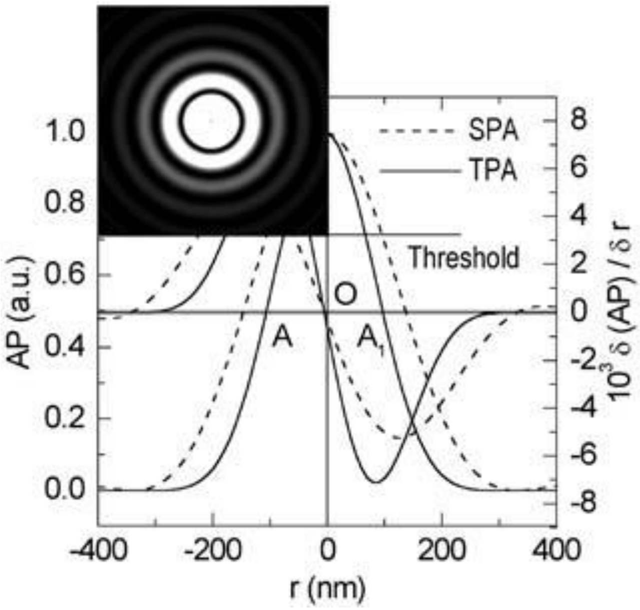

Fig. 2. Light intensity analysis for understanding the achievement of sub-diffraction-limit spatial resolution. Focal plane light intensity (dashed line) and the square of light intensity (solid line) distribution are associated with single-photon and two-photon excitation, respectively. Their derivative distribution is also shown. The inset is the diffraction pattern at the focal plane [5]

7.3. Metal Structures using Two Photon Polymerization

Recently several techniques have been developed to create freestanding metal nanostructures using a two photon polymerization process. In the first technique 3D polymer structures created using two photon polymerization have been coated with silver [6]. In the second technique metallic structures have been created by using a polymer nanocomposite designed to nucleate and grow metal nanostructures [7].

Since surface charges are responsible for the actuating properties of nanoporous metals these materials do not need to be solid metal. One method of creating ordered nanoporous metals is to coat a 3D polymer structure. In this procedure 3D nanostructures are created from a polymer by two photon polymerization. The structures are then coated to create a metallic structure. It is important that the deposition rate of the metal coating be controllable. This allows a uniform coating to be applied to the polymer avoiding filling of the eternal cavities. To control the deposition rate of the metal coating, the polymer structure is first functionalized with alkylamines creating surface bound amine terminated amides. Gold particles are then bound to the amines and these particles serve as nucleation sites for electrodeless deposition of silver. As a result, the silver layer thickness is controlled through the immersion time in the electrodeless deposition process. A schematic of the silver deposition process is shown in Figure 3 [6].

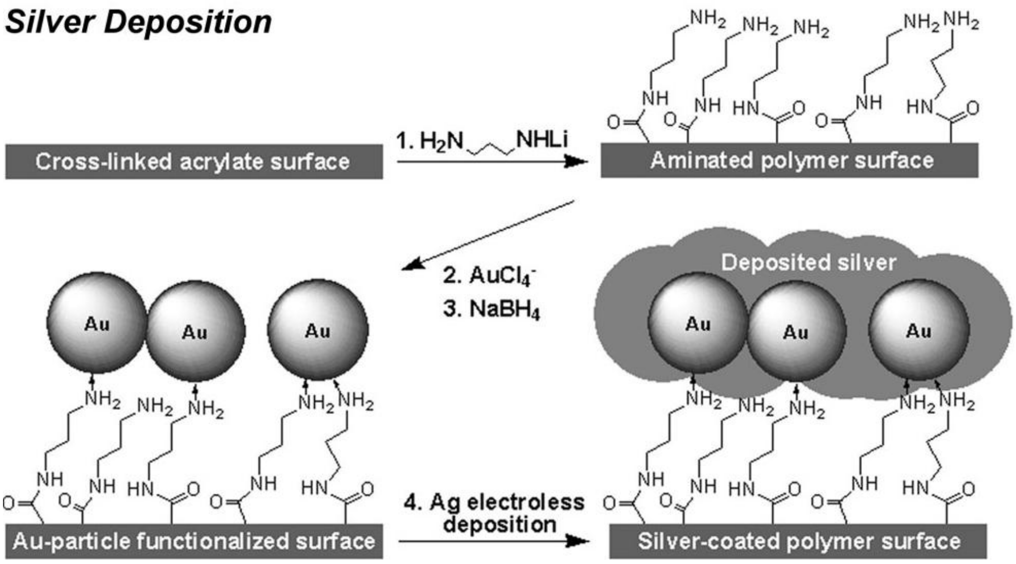

Fig. 3. Schematic of silver deposition process. The surface of the polymeric scaffold is aminated with NH2(CH2)3NHLi, then Au3+ is bound at the amine sites and reduced with NaBH4 (aqueous). The resulting surface-bound gold particles nucleate electrodeless deposition of silver onto the polymeric microstructure [6]

Pure metal structures have been fabricated by two photon polymerization through the use of a carefully designed nanopolymer composite. In this process two photon absorption by a photosensitive dye is used to generate silver ions from a silver salt through electron transfer. These silver ions are then free to combine with another silver ion to nucleate or join an existing particle. The formation and growth of metal structures will depend on the competition between the rate of nucleation and growth [7]. Control over the nucleation rate can be achieved by introducing ligand coated silver seed crystals into the polymer composite. These seed crystals will serve as controllable nucleation sites for the growth of the silver nanostructures. An example of a gold microstructure fabricated using a similar nanopolymer composite is shown in Figure 4 [7].

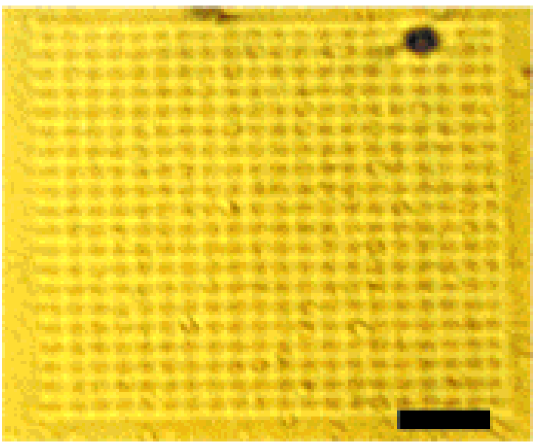

Fig. 4. TOM image of a gold microstructure fabricated by two photon laser exposure. Scale bar 25 μm [7]

7.4. 3D Structures Using Interference Effects

The metallic structures created using two photon polymerization to date do not have a high enough surface to volume ration to be used as actuators. Utilizing interference effects of multiple laser beams could be one method to create metallic structures with high surface to volume ratios. In this technique the diffraction pattern from multiple laser beams is used to create a 3D structure instead of layer by layer rastering of a single laser beam.

Using a four laser beam setup complex polymer 3D structures with translational symmetry have been created [8]. The translational symmetry and lattice constant of the interference pattern are determined by the wavevectors of the four laser beams. The intensity distribution within the unit cell is determined by the intensity and polarization vectors of the laser beams. The large number of adjustable parameters allows for a variety of structures to be generated. An example of an f.c.c. pattern formed by constant intensity surfaces of a four beam laser interference pattern is shown in Figure 5 [8].

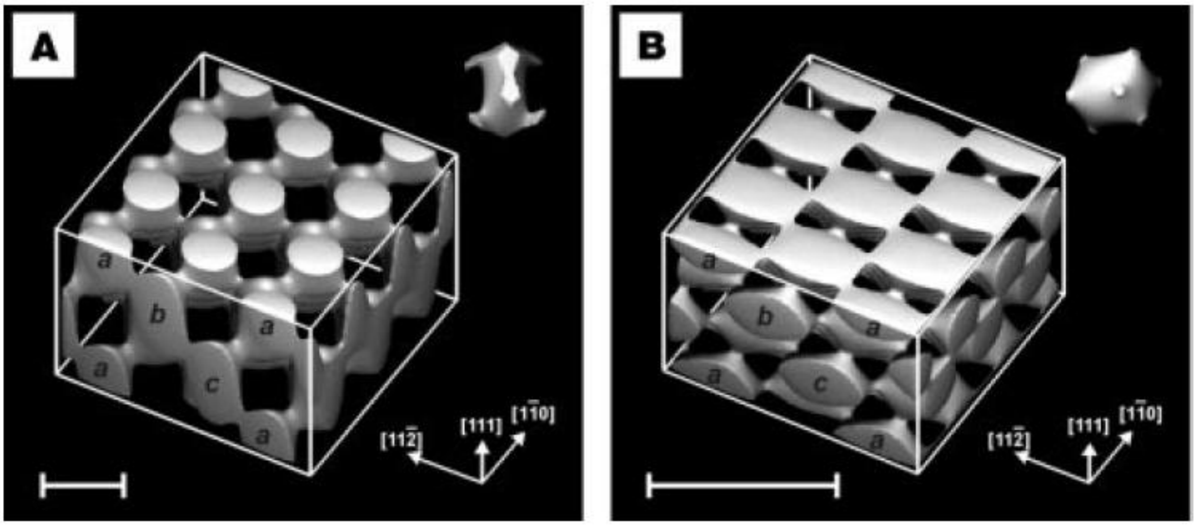

Fig 5. Calculated constant-intensity surfaces in four-beam laser interference patterns designed to produce photonic crystals for the visible spectrum from photoresist. The primitive basis (contents of a Wigner-Seitz unit cell) is shown inset in each case. A, f.c.c. pattern with lattice constant 922 nm. The close-packed layers of the f.c.c. lattice are indicated on one side of the cube. B, f.c.c. pattern with lattice constant 397 nm. Scale bars, 500 nm [8].

7.5. Incorporation of Solid Electrolyte

Current ordered nanoporous metals use a liquid electrolyte to charge the metal surface. Although for some applications a liquid electrolyte is preferable the majority of applications require a solid electrolyte. A liquid electrolyte will easily fill the entire structure providing allowing actuation over the entire surface area of the nanoporous metal. The challenge of using a solid electrolyte is to achieve filling of the entire structure so that the entire surface area of the metal will provide a mechanical response to an applied charge.

Over the past decade much research has been devoted to developing solid polymer electrolytes for batteries and fuel cells. A recently reported polymer electrolyte utilizing silver salts for ionic conduction is a promising candidate for use with ordered nanoporous metal actuators. This polymer consists of silver salts contained within a graft copolymer. The graft copolymer has two components,poly(oxyethylene)$_9$ methacrylat (POEM) and poly(dimethyl siloxane) (PDMS). The two polymers phase separate forming microdomains. The POEM contains 9 ethylene oxide groups which will trap silver ions and provides the ion conduction [9].

Such a polymer electrolyte could be used for a solid electrolyte for the nanoporous metallic structures mentioned above. The idea is to replace the polymer backbone used in the nanocomposite blend with the graft copolymer. In this way the precursor polymer blend will be a solid electrolyte so any non-exposed region will act as the electrolyte; eliminating the need to try and incorporate the electrolyte after the metallic structures are created.

The problem with this technique is that the POEM traps the silver ions inside a ethylene oxide cage. Although this is needed for ionic conduction it could prevent the nucleation and growth of the silver structures during the two photon polymerization process. However, research has shown that different silver salts have a different affinity for incorporation into the POEM microdomains. The affinity of two silver salts, $AgClO_4$ and $AgCF_3SO_3$, can be seen by examining Figure 6 which show the glass transition temperature T_g as a function of the [Ag]/[EO] ratio. For each salt T_g increased with increasing [Ag]/[EO] ratio before saturating around 0.20. The presence of silver ions in the POEM restricts the mobility of the polymer chains causing the increase in T_g. It is clear from Figure XXX that the T_g of $AgClO_4$ is always higher than that of $AgCF_3SO_3$. This lead one to conclude that for the same [Ag]/[EO] ratio the $AgClO_4$ incorperates more ions into the POEM. This means that the $AgClO_4$ has a higher affinity for the POEM polymer than $AgCF_3SO_3$.

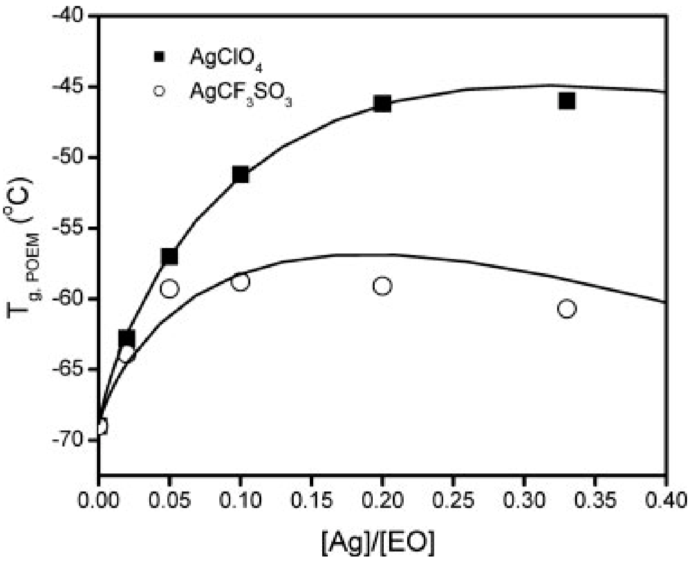

Figure 6. T_g of the POEM as a function of [Ag]/[EO] ratio for $AgClO_4$ and $AgCF_3SO_3$ [9].

For the polymer electrolyte to be used to grow the ordered nanoporous metals the silver salt should have a low enough electron affinity with the polymer so that the silver ions are free to nucleate and grow during laser exposure while still having a strong enough interaction to have good ionic conductivity in the unexposed regions. Therefore the performance of many silver salts will need to be investigated to find a silver salt with the right affinity for the POEM.

In addition to how the graft copolymer will affect the growth of the metallic nanostrucuteres it is not clear how the other components in the polymer nanocomposite, such as the seed crystals and the photosensitizing dye, will affect the properties of the electrolyte. As such, the ionic conductivity of the polymer electrolyte will need to be tested as a function of the concentration of the various composite comments.

7.6. Project Aim

This project will investigate the use of the two photon polymerization process for creating nanoporous metals which are ordered on the nanoscale for use as mechanical actuators. Current processing techniques using two photon polymerization have been used to create 3D metallic nanostructures. However, these structures do not have high enough surface to volume ratios to be considered true nanoporous materials. On a separate front two photon polymerization using interference effects of multiple laser beams have been used to create polymer lattices with filing factors of 34%-79% [8], which would constitute a nanoporous material. This technique has been used to create photonic crystals and has not been utilized for development of ordered nanoporous metals.

To achieve this aim the project is broken down into a series of task. In the first year the PhD student will concentrate on producing 3D metallic nanostructures using the two processes described above. Structures made with each technique will be analyzed to determine which technique will produce metallic structures with superior properties for use as mechanical actuators.

Characterization of the metallic structures produced will be done using several techniques. Examination of the crystal orientation of the metal will be done using TEM and SEM. This will provided information about the quality of the metal grown by the different techniques. Measurement of the actuating properties will be done by immersing the samples in aqueous electrolyte solutions and displacement as a function of applied voltage will be determined with dilatometry.

In the second year the PhD student will work to incorporate the technique chosen in the first year with the multiple beam interference technique. During this time the PhD student will experiment with different inference patterns to create varying structures. These structures will then be analyzed to determine the relationship between the structure of the nanoporous metal and its actuating properties.

Characterizations of the structures produced by the interference patters will be done using diffraction techniques as well as SEM and TEM. The diffraction techniques include small angle x-ray scattering and convergent beam electron diffraction. The actuating properties of the different structures will be characterized using dilatometry.

In the third year of the project the PhD will look to combine a solid electrolyte into the processing of the nanoporous metals. The PhD student will experiment with a solid electrolytes with different silver salts to see if any can be integrated into the processing procedure developed in the preceding years and if so what are the properties of the actuators created. Dilatometry will again be used to determine the effect the solid electrolyte will have on the performance of the actuators.

The final year of the project will be devoted to finishing the proposed experiments and writing a PhD thesis.

8. Infrastructure

The IR femtosecond laser and optical components needed for the two photon polymerization process will need to be purchased. The optical equipment needed for the 3D interference process include half-way plates and dielectric polarizing beamsplitters in addition to the standard optical components such as mirrors and focusing lenses. All of the characterization equipment needed for this project are present within the Materials Science group at the Zernike Institute for Advanced Materials.

9. Application Perspective

As previously mentioned nanoporous metal actuators can achieve similar mechanical stresses as current ceramic materials at voltages up two order of magnitude smaller. However, nanoporous metals have other advantages over their ceramic counterparts.

In actuating ceramics the strain is the result of atomic rearrangements and is therefore a material property. For nanoporous metals the induced strain caused by a change in the surface properties of the metal. As a result, the properties of the metal actuator will depend on the surface to volume ratio and its structure. Using the two photon polymerization process the structure of the nanoporous metal is easily changed by exposing a different region of the polymer precursor. This will allow for nanoporous metal actuators with different performance properties to be easily created by only adjusting the laser optics and not the composition of the material. In addition, the two photon polymerization process allows large areas to exposed at once [10] creating either large nanoporous metal actuators or many small ones which is useful for industry.

Currently the use of liquid electrolytes limits the use of nanoporous metal actuators. The incorporation of a solid electrolyte is essential if this type of actuator is to become useful for widespread technological applications. The proposed method to create a polymer electrolyte precursor would eliminate the difficulty of trying to infuse the nanoporous metal with a solid electrolyte. This would open the way for nanoporous metal to be used in many more technological applications.

10. References

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