



Research Paper

A nanoporous gold-polypyrrole hybrid nanomaterial for actuation

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ABSTRACT

We discuss actuation with a hybrid nanomaterial that is made by electro-polymerizing pyrrole on the internal surfaces of dealloying-derived nanoporous gold and then letting aqueous electrolyte be imbibed in the remaining pore space. In this way, active polypyrrole films are contacted by two separate but individually contiguous conduction paths, providing efficient transport of ions in the electrolyte channels and of electrons in the metal skeleton. The metal skeleton also serves to enhance the mechanical behavior of the actuator. Actuation exploits the dimension changes of the polymer when ions are exchanged with the electrolyte in a pseudo-capacitive way, at potentials negative of the classic oxidation/reduction of polypyrrole. Our experiments with millimeter-size bulk samples indicate fast switching and substantially larger strain amplitude than nanoporous metal actuators.

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1. Introduction

Among materials for actuation, low-voltage electrochemical systems utilizing conducting polymers receive considerable attention [1,2]. The low voltage is safe, compatible with battery sources, and power input is potentially low [3]. Conducting polymers in contact with electrolyte can be oxidized or reduced by anodic or cathodic current. Ions and solvent are exchanged during these reaction, so that charge and osmotic pressure remain balanced. The composition variation is not only coupled to charge storage, but also to a volume change [4,5]. Thus, conducting polymer actuators exploit the coupling between the electric charge and mechanical strain during electrochemical processes that require low applied potentials [2,4,6,7]. As a drawback, rates of actuation tend to be low because of the relatively slow transport of ions within the polymer [6,8]. Thin film geometries, for instance in “ionic polymer metal composites” improve the kinetics, yet at the expense of large compliance [6]. Furthermore, the performance of conducting polymer actuators can be restricted by creep [3,9] and by the low stress that is sustained during actuation [3,10–12]. Here, we explore polypyrrole (PPy), a well investigated electroactive polymer system [13]. Exploiting a strategy that has been demonstrated for application as supercapacitors [14,15], we structure the PPy so that it contains separate conduction channels for ions as well electrons, interspersed at submicron scale. At the same time, we

incorporate a mechanically robust metallic skeleton phase which enhances strength and stiffness.

Nanoporous metals made by dealloying [16–18] take the form of monolithic, millimeter sized bodies that consist of a homogeneously interconnected network of nanoscale ‘ligaments’ and pore channels with a characteristic size that can be controlled down to well below 10 nm [19–21]. Nanoporous gold (NPG) provides a model system for dealloying-made metal nanostructures because of the material’s particularly reproducible synthesis and its highly uniform microstructure. Due to size-effects, the ligaments that make up the metal skeleton are locally very strong. Thus, even though NPG is highly porous, significant values of the stiffness and of the effective macroscopic yield strength have been reported [22–26]. The mechanical performance is greatly enhanced when the pore space is filled with polymer, such as epoxy resin [27,28]. This observation suggests that NPG decorated with PPy as the active component might provide a hybrid nanomaterial that compromises between the large actuation amplitude of PPy and the good mechanical properties of metal nanomaterials.

Actuation is well documented for nanoporous metals with no PPy component [29–33]. When the pore space is filled with aqueous electrolyte, the materials actuate under electrochemical control of their surface stress [34,35]. This has been demonstrated for nanoporous gold [20,36], platinum [29,37], silver [32], nickel [33], palladium [38] and nanoporous Au-Pt alloy [21]. The materials are distinguished by their good electronic conductivity and by their strength and stiffness. On the other hand, strain amplitudes are considerably less than in polymer actuators and might benefit from enhancement.

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Hybrid materials made from NPG and conducting polymer have already been demonstrated in the contexts of charge storage and sensing. Meng et al. [14] explored thin films of PPy-decorated NPG as electrochemical supercapacitors with high power and energy density. In the same context, Lang et al. [15] investigated NPG-polyaniline hybrid films. Xiao et al. [39] reported a hybrid film made by electropolymerizing 3,4-ethylenedioxythiophene on NPG for applications as biosensors. Detsi et al. [40] presented a electrolyte-free actuation in a NPG-polyaniline hybrid material, again in thin-film form, emphasizing the high actuation strain rate of the material.

Here, we explore the NPG-polypyrrole system for actuation, with a specific focus on making not thin films but macroscopic, monolithic actuator materials. We show that by functionalizing the gold-electrolyte interface with thin PPy layers the actuation amplitude of the material can be strongly enhanced compared to actuation with pure NPG. At the same time, switching response times are found substantially faster than in bulk actuators from conductive polymers without the interpenetrating metal skeleton.

2. Material and methods

Cylindrically shaped NPG samples with diameter 0.9 mm and length of 1.5 mm were prepared by following the procedures in Ref. [28]. The Au₂₅Ag₇₅ master alloy was prepared by arc-melting, homogenized by annealing for 100 h at 850 °C, shaped to a cylinder by wire drawing and finally annealed in vacuum during 3 h at 650 °C for recovery.

The master alloy samples were dealloyed in 1 M HClO₄ prepared from HClO₄ (Suprapur R, Merck) and ultrapure water (18.2 MΩ cm) at dealloying potential 0.75 V and ambient temperature. When the current fell to below 10 μA, the potential was stepped to 0.85 V and held for 3 h, which completed the dealloying. In order to remove surface and subsurface oxides, the samples were then subjected to 40 potential cycles in the interval 0–1.0 V at scan rate of 10 mVs⁻¹ [20]. Immersion in ultrapure water and drying in vacuum for 3 days followed. All samples were then annealed at 300 °C in air for 1 h to increase the ligament size. Energy dispersive x-ray spectroscopy in the scanning electron microscope (SEM) suggests that the resulting nanoporous material is essentially pure Au, with a residual Ag content of ≤2 at.-% [27].

With the exception of the electropolymerization (see below), all electrochemical experiments in this work used Ag/AgCl pseudo-reference electrodes, and all respective potentials are specified versus this electrode. The reference potential was measured as +0.202 V vs. versus an Ag/AgCl electrode in saturated KCl solution (World Precision Instruments, Inc., which is itself +200 mV vs. the standard hydrogen electrode, SHE). Thus, our potentials are shifted by +0.402 V versus SHE.

Bulk samples of nanoporous gold-polypyrrole (NPG-PPy) hybrid material were made by electrochemical polymerization of pyrrole in NPG. The commercial pyrrole monomer (Sigma-Aldrich) was purified by passing through a column of basic alumina and stored in a dark bottle at 4 °C. Commercial anhydrous LiClO₄ (Merck) and HPLC grade acetonitrile (Sigma-Aldrich) was used as received. The electrolyte solution was 0.1 M pyrrole and 0.1 M LiClO₄ in acetonitrile containing 2% water. In a three-electrode setup a Pt wire served as counter electrode and a saturated calomel electrode (SCE, World Precision Instruments) as reference electrode. Bulk NPG samples were used as the working electrode and firstly immersed into the electrolyte solution for ½ h. The polymerization of pyrrole to PPy used consecutive square waves of potential between –500 mV (2 s) and +800 mV (8 s) for 450, 900 and 2200 cycles, which needed in total around 1.25, 2.5 and 6 h, respectively. The hybrid material were then rinsed thoroughly with ultrapure water.

The electrochemical behavior of the hybrid material was characterized in 1 M HClO₄ aqueous electrolyte by three-electrode cyclic voltammetry at scan rates of 10 mV s⁻¹. Actuation measurements, also in 1 M HClO₄, used an *in-situ*, electrochemical cell inserted in a dynamic mechanical analyzer (DMA; BOSE ElectroForce), in combination with a potentiostat (Autolab). Fig. 1 illustrates the setup. Prior to all measurements the glassware was cleaned in Piranha solution and rinsed with ultrapure water. Carbon cloth served as counter electrode.

A scanning electron microscope (SEM; LEO 1530 Gemini) operated at 10 kV was used for characterization of microstructure and composition. Compression tests used a Zwick 1484 testing machine with the elongation measured between the load surfaces. A feedback loop controlled and progressively reduced the crosshead speed so as to maintain constant true strain rate at 10⁻⁴ s⁻¹ while the sample length varied.

3. Results

3.1. Microstructure

SEM images prior to polymer decoration (Fig. 2A) illustrate the bicontinuous structure of NPG and the ligament size in our samples, $L = 250 \pm 50$ nm. In this first study we selected the comparatively large L in order to assure sufficient transport channel cross-section for easy monomer transport during polymerization and for fast ion transport during actuation.

The success of electrochemical polymerization of pyrrole is demonstrated in Fig. 2(B), which shows the fracture cross-section SEM micrograph of NPG-PPy hybrid material. A conformal coating of the ligaments with PPy, 80 nm thick, is apparent. The electropolymerization exploits the good adsorption of pyrrole monomers on gold surfaces and the high electrical conductivity of NPG electrodes [14]. The homogeneous PPy layer thickness, throughout the bulk nanoporous sample, suggests that attachment kinetics may limit the growth rate. The thickness of PPy layer for NPG-PPy hybrid nanomaterial can be tuned by adjusting the time, t_p , of the potentiodynamic polymerization. Hybrid nanomaterial with PPy layers of thickness 15 ± 5 nm ($t_p = 1.25$ h), 50 ± 10 nm (2.5 h) and 80 ± 20 nm (6 h) are shown in Fig. 2(C)–(E), respectively.

3.2. Electrochemical characterization

Fig. 3 summarizes electrochemical properties of pure NPG and NPG-PPy composite characterized by cyclic voltammograms in 1 M HClO₄. The dashed graphs in part (A) of the figure refer to pure NPG; note the distinct oxygen adsorption and desorption peaks with their onsets at around 0.8 V. The oxygen-on-gold electroadsorption features are missing in the CVs of the NPG-PPy hybrid nanomaterial (solid lines). This shows that the gold surface is indeed completely coated by PPy. The prevailing feature of the CVs on the hybrid nanomaterials is an apparent adsorption peak with an onset at 0.91 V, and a corresponding desorption peak that is shifted substantially to negative potentials, with an onset at 0.75 V. This behavior is similar to earlier reports on voltammetry for PPy [41]. A shift of the electroadsorption peak in our scans to positive potential, as compared to published data, may be rationalized as the consequence of the pH-dependent potential [42] along with the acidic nature (pH ~ 1) of our electrolyte. The figure shows that repeated cycling to an upper potential vertex of 1.2 V leads to a slight decrease of the PPy-related peaks, while no oxygen-on-gold electroadsorption feature appears.

Part B of Fig. 3 shows CVs in a larger potential interval. As the most obvious feature, the current increases drastically at the upper end of the potential scale, and the voltammogram degrades severely during the 10 cycles of the figure. Most remarkably, the

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