Improved charging and strain rates by laser perforating polypyrrole actuator electrodes

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Abstract
Conducting polymer actuators generate significant strains (1%–10%) when driven at low voltages, and are muscle-like in their linear deformation, mechanical compliance, silent operation, and energy density. However, slow electrochemical processes have hindered widespread application. To operate electroactive polymer actuators in practical applications such as soft robotics, the speed of energy delivery is often important. Recent work has achieved very fast actuation by using very thin films and blending of materials of high ionic conductivity with conducting polymers, allowing fast insertion of ions. Here we make microscopic arrays of holes in relatively thick, easy to handle conducting polymer films in order to speed ion insertion and actuation. A single-step, top-down, non-contact and template-free approach is used, employing femto and picosecond lasers to texturize polypyrrole based actuators while preserving the stress and strain output. A wide range of hole separations and diameters (pitch/diameter from 9.75/5.17 \( \mu \)m to 24.7/13.2 \( \mu \)m) are explored to reduce the ion diffusion path length in the bulk polymer. This led to a speed increase of between 2 and 30 times. A finite element model based on diffusion shows similar improvements, suggesting that the reduced distance of mass transport achieved by laser perforation is the key to faster response times in the thick electrodes used. The demonstrated ability to increase rate of response using micromachined electrodes is potentially applicable to batteries and supercapacitors.

Keywords: ultrafast laser, template-free micro-structuring, electroactive polymer actuators, artificial muscle, energy storage

(Some figures may appear in colour only in the online journal)

1. Introduction
Among the emerging actuators, electroactive polymers such as polypyrrole (PPy) possess attractive characteristics including large strain outputs (typically 2%–8%), low operating voltage (\( \pm 2 \) V), and ease of fabrication and potential for miniaturization [1]. Ionic electroactive polymers base their operation on the electrochemically induced intercalation of free ions and solvent molecules into the bulk, causing reversible volumetric expansion and contraction. Owing to the large uptake of ions (~1 per every 3 monomers), electroactive polymers typically have large electrical energy densities. A consequence of the high charge and energy densities is a significant volume change upon charging and discharging—with the volume change being proportional to the amount of charge transferred. However,
relatively a lot of charge needs to be inserted in order to achieve actuation. A major drawback of the electroactive actuators is their slow speed of electrochemical actuation, which is limited by the characteristic length of the effective ion diffusion path into the polymer, as well as internal resistances. The strain rate can be increased by increasing the magnitude of the applied potential, but this can lead to polymer degradation [2] if compensation is not applied [3]. Other methods of increasing the strain rate are to reduce the ion diffusion path by using thinner and/or more porous films and fibers [4, 5] or to increase ion mobility by employing smaller dopant molecules [6].

It has been proposed that a network of electrolyte-filled macropores in PPy can reduce the ion diffusion paths in the polymer and improve the actuator’s electrochemical strain rate [7]. A number of fabrication methods developed to create micro- or nanoporous polypyrrole structures have been exploited for enhancing polypyrrole charging rate performance in various [8–13]. These fabrication methods are multi-step and bottom-up approaches that electrochemically grow polypyrrole onto a conducting template or scaffold (carbon fiber scaffolds, inverse opals, etc) resulting in sponge-like structures. In some cases, where the template materials are left behind, the resulting materials are too stiff (due to a carbon fiber or other scaffold that remains). In this work, we show a direct machining process, rather than a templating process, works to dramatically improve rate of response. This direct machining process may be more practical in certain applications—for example if used in any case to pattern cylindrical electrodes on the surface of an actively deformable catheter.

A particularly exciting method of dramatically improving rate of charging and actuation has resulted in a bandwidth of 60 Hz (for square wave activation) and a resonant response approaching 1 kHz [14]. In this approach, a composite structure is created, consisting of an electronically conducting polymer, a highly ionically conductive polymer and an elastomer, that interpenetrate at the nanometer scale [15]. In this case the conducting polymer is poly(3,4 ethylenedioxythiophene (PEDOT), which is mixed with polyethyleneoxide for its high ionic conductivity (when filled with electrolyte) and nitrile butadiene rubber for its excellent mechanical extensibility. The 60 Hz response was obtained in a trilayer (bending) actuator, with each active layer containing PEDOT being about 2 μm thick. This thickness is important as the frequency response goes up as the inverse square of the thickness, when diffusion-like transport is the rate limiting factor.

In this work we study an alternative for rapidly inserting ions into the polymer in which a laser is used to drill holes. Material processing with an ultrafast direct laser writing technique provides a single-step, top-down, non-contact and template-free methods of structuring material surfaces or near-surface volumes, enabling the modification of physical material properties for enhanced surface functionalities [16–19]. By focusing the laser beam to create high intensity in the material, feature sizes on a ‘macro’ scale (dimensions ≥0.1 mm) and in the ‘micro’ range (structural width <0.1 mm) can be created while leaving the bulk material unaffected [20]. In comparison to nanosecond and longer pulse duration lasers, ultrashort laser with pico- or femtosecond pulse duration offer higher peak intensity to drive stronger laser material interaction and greater interaction confinement with smaller heat- and shock-affected zones. Hence, ultrafast laser micro-structuring of polypyrrole with organized arrays of microholes is explored here in order to enhance the electrochemical charging and actuation rates of polypyrrole actuators.

Here we propose an approach to increase the rate of ion diffusion by perforating the polypyrrole actuator using femtosecond laser ablation. It builds on previous work from our group in which laser machining was used to machine a polypyrrole layer. The layer uniformly coated a commercial catheter. The laser ablation divided this coating into four quadrants, enabling independent actuation of pairs of electrodes, in turn enabling bending of the tip in two-dimensions [21]. A laser perforation technique was subsequently refined and reported, describing the conditions needed in order to achieve micromachining of polypyrrole with reproducible perforations of uniform depth [22]. Meanwhile we also investigated the use of electrical discharge machining to pattern polypyrrole into electrodes, again on a cylindrical commercial catheter [23]. What has not been reported by any of the contributions, and is the objective of this current study, is the quantitative investigation of the effect of laser perforation parameters in polypyrrole actuators in order to obtain quicker transport of ions, more rapid charging and faster actuation. In the present work we describe the fabrication and electromechanical characterization of ultrafast laser micro-patterned polypyrrole actuators and characterize the rate of response as the hole diameters and pitches are systematically varied. Numerical modeling of the texturized actuators is performed to confirm the empirical results, including the shortened time constants of actuation due to shortened diffusion distances.

2. Experimental methods and numerical analyses

Uniform sheets of polypyrrole were synthesized electrochemically and perforated using a femto/pico second laser at various diameters and pitches. The fidelity of laser patterning was optically confirmed and further inspected via SEM to visualize the anisotropy (i.e. without a significant lateral propagation of the laser-induced shock) of the perforated holes. The internal electrochemical capacitances and associated time constants of the uniform and laser-texturized samples were determined via cyclic voltammetry (CV). Finally, actuation tests were performed by applying 0.6 V square wave perturbations (versus Ag/AgCl) of various frequencies to correlate the ion diffusion path lengths and the actuation speeds, as modulated by the amount of volume removed by the laser.

2.1. Electrochemical synthesis of freestanding polypyrrole films

Polypyrrole films were deposited by polymerizing pyrrole monomer through electrochemical oxidation following the
method of Yamaura et al [24]. A solution of 0.06 M distilled pyrrole (Aldrich) and 0.05 M tetraethylammoniumhexafluorophosphate (TEAPF₆, Aldrich) in propylene carbonate (PC, Aldrich) containing 1% by volume of deionized water was deoxygenated by bubbling with nitrogen before growth. A polished glassy carbon substrate was used as the working electrode, and a platinum coated glass slide as the counter electrode. The polymerization reaction was driven at constant current of 0.125 mA cm⁻² and held at a temperature of −30°C for 12 h to obtain a polymer thickness of approximately 27 μm.

2.2. Ultrafast laser micropatterning

The surface of the uniform polypyrrole film was textured with a femtosecond laser (300 fs, 522 nm, 100 kHz) and a picosecond laser (12 ps, 532 nm, 200 kHz). Several ‘parent films’ of polypyrrole were synthesized, from which multiple batches of perforated samples were generated by cutting and laser patterning. An aspheric lens of 11 mm focal length (5725HA, New Focus) focused the Gaussian-shaped femtosecond laser beam to a diffraction-limited spot size of 5.6 μm diameter (1/e²) onto the sample surface. Based on previously reported laser exposure conditions [22], a laser fluence of 400 μJ cm⁻² and 100 exposure pulses per spot were used to obtain through holes in 27 μm thick PPy film. An acousto-optic modulator controlled the laser firing during an XY raster scan of a motion stage. This resulted in the ablation of hexagonal arrays of microholes in a 10 mm × 1 mm region. For each array that was created, a particular hole diameter and pitch were used. The diameters ranged between 4.5 and 9 μm and pitches between 6 and 25 μm. Pitch was chosen to be less than or approximately equal to the film thickness, ensuring that lateral diffusion distances were always shorter than that of the through-film direction—leading to an improvement in charging speed.

During drilling, laser fluence and number of exposure pulses were kept fixed. Different hole diameters were obtained by changing the laser focusing condition either with objective lenses of different numerical aperture or with the defocusing technique. The femtosecond fiber laser had a maximum pulse energy of 700 nJ at the lowest repetition rate of 100 kHz, which turned out to limit the laser fluence and the largest diameter obtainable under this exposure condition to ~9 μm. While it is possible to increase the hole size by increasing the number of exposure pulses, a proportional decrease in the laser scan speed is required to ensure proper overlap of laser pulses, resulting in a long processing time of >8 h for a 10 mm² area, which was deemed impractical for large area patterning. Hence, a high power industrial 12 ps laser (HYPER RAPID 50, Lumera) was applied to more effectively ablate hole diameters between 10 and 24 μm.

2.3. Electrochemical characterization

Electrochemical characterization including CV and potential square wave perturbation (for actuation observation) was performed in 1.0 M NaPF₆ aqueous electrolyte against an Ag/AgCl reference electrode (BASI) and a large PPy film as the counter electrode, as shown in figure 6(a). All electrochemical characterizations were done using the potentiostat WN50-BASIC (Pine Research Instrumentation).

Freestanding films of polypyrrole, with dimensions of 10 mm × 1 mm × 27 μm were used as the working electrode for CV with a scanning rate of 2 mV s⁻¹ between ±200 mV versus Ag/AgCl in 1 M NaPF₆ aqueous electrolyte. From the CV curves, the capacitances of the polypyrrole films were estimated by dividing the saturation current by the scan rate, for films in which a steady current was reached.

2.4. Actuation tests (potential square waves)

Each 10 mm × 1 mm × 27 μm polypyrrole film was made into a bi-layer actuator by bonding with Kapton tape as the passive non-permeable layer. The bilayer structures were driven with ±0.6 V versus Ag/AgCl square waves in 1 M NaPF₆ aqueous electrolyte. This voltage was used to drive a fast actuation response while staying within the range of safe operating voltage from −0.4 V to +0.8 V (versus Ag/AgCl) to prevent polymer degradation [2]. To record dynamic bending, a digital video camera was pointed orthogonal to the actuator’s bending direction as illustrated by the superimposed optical images in figure 6(a), showing an actuator in both the neutral position and the maximum bent position with a bend radius, R. Also visible in the camera’s field of view were the Ag/AgCl reference electrode and a large freestanding PPy film as the counter electrode in close proximity to the actuator in order to minimize electric potential drop across the aqueous solution. Image analysis consisting of thresholding, conversion to black and white, and skeletonization was performed using MATLAB (Natick, MA) to extract the tip deflection as a function of time, from which the rise time and maximum curvature were obtained to evaluate and compare actuator performance.

2.5. Visual analyses

To demonstrate the high fidelity of the direct laser writing technique of the well-organized hexagonal pattern of microholes, optical microscope images of the femtosecond laser-micropatterned polypyrrole films were taken with top and bottom illumination, where hole pitches of 12, 8 and 18 μm were applied while keeping constant a diameter of ~6.2 μm.

To examine and compare the cross section profiles of the holes ablated with both femto- and picosecond lasers, the laser-texture polypyrrole films were laser cut through the microhole array and the exposed facets were imaged with a scanning electron microscope (S-5200, Hitachi).

2.6. Finite element simulation

COMSOL Multiphysics (Stockholm, Sweden) was used to perform finite element analyses of the texturized polypyrrole actuators. The model was built on the thermo-elastic model demonstrated by Spinks et al [25]. Drawing on the analog between ion-induced and thermal-induced strain, the thermoelastic model mimicked the rate of propagation of the ion
migration into the polypyrrole layer with a temperature distribution model. The temperature was then linearly related to the active strain through the material’s thermal expansion coefficient, \( \alpha \), which was adjusted together with Young’s moduli of polypyrrole and the substrate to best fit the theoretical bending angles and moments to those observed experimentally. The structure models a planar bi-layer bending actuator. By assuming similar lateral ion diffusion behavior in the organized microhole array, the model geometry was further simplified to a narrow length-wise actuator strip that contains a single-file line of microholes. This linear geometry does not account for the hexagonal arrangement of holes, and so overestimates the diffusion distance. This may explain why in some cases the experimental rise times are shorter than the measured times. Figure 3(a) shows the planar geometry used to model the actuation response of a 27 \( \mu \)m thick uniform polypyrrole bi-layer actuator. This polypyrrole thickness was selected to match the fabricated film thickness. The Kapton tape was composed of a 25.4 \( \mu \)m thick polyimide and a 31.7 \( \mu \)m thick silicone adhesive layer. Young’s moduli of 350, 1 and 2500 MPa were used for the polypyrrole, silicone and polyimide layers, respectively, as reported in the literature [26].

A virtual conducting layer with an ‘electron’ thermal diffusivity of \( D_e \) was added to the upper surface of the polypyrrole layer to simulate electron propagation down the length of the actuator away from the electrical contact as indicated by the red line in figure 3(a). A stepwise increase/decrease in temperature, representing voltage, is applied to the left-hand corner of this contact. The Young’s modulus and thickness of 1 MPa and 5.4 \( \mu \)m, respectively, were selected for this virtual layer to minimize its mechanical stiffness and therefore not impede the bending of the actuator model.

3. Results and discussions

3.1. Ultrafast laser micropatterning

Selected optical microscope images of the femtosecond laser-micropatterned polypyrrole films are shown with top illumination in figure 1 parts (a), (c) and (e), and the corresponding bottom illumination in figures 1(b), (d) and (f), respectively, where hole pitches of 12, 8 and 18 \( \mu \)m were applied while keeping constant a diameter of \( \sim 6.2 \mu \)m. The high fidelity of the direct laser writing technique is demonstrated by the well-organized hexagonal pattern of microholes, where, in the bottom-illuminated images, spots of transmitted light confirm that the films were indeed penetrated.

Figure 2 parts (a) and (b) show the top view of SEM micrographs of a femtosecond and a picosecond laser-textured films, respectively, with the corresponding angled views of the laser-cut facets shown in figures 2(c) and (d). The asymmetry in laser beam shapes together with imperfect overlapping of laser pulses during laser raster scanning resulted in the oblong hole shapes. Nonetheless, pristine through holes with minimal tapering and collateral damage were observed in both films in the expanded views (insets) of figures 2(c) and (d). The similarity between hole qualities obtained with both lasers suggested the 12 ps laser as a suitable alternative for processing PPy films.

As established in [21], the main mechanism of ablation is by vaporization and not melting, hence the impact on polymer’s electrical property is minimized. This was true for fs-laser patterned PPy. The same inference was reached for ps-laser patterned PPy by comparing the optical images of the ps-laser and fs-laser patterned samples.

3.2. Finite element modeling of the micropatterned actuators

Charging and actuation were simulated in both the original polypyrrole and the perforated polypyrrole films. After the application of a change in temperature to one side of the contact (to simulate a change in voltage), the rising temperature first
came into contact with the polypyrrole layer that has a lower ‘ion’ thermal diffusivity of $D_i$, simulating the slow ion diffusion through the polymer thickness and, in the case of perforated structures, laterally through the sidewalls of the microholes. This active polypyrrole layer was also the only layer with a non-zero thermal expansion coefficient of $\alpha$, that caused the polypyrrole layer to expand or contract against the passive substrate layer (i.e. Kapton tape)—resulting in bending.

The model parameters were first fit based on physical observation. The entire model was set to an initial temperature of 300 K. To stimulate expansion in the polypyrrole layer, a higher temperature of 400 K was arbitrarily selected and applied to the edge of the virtual conducting layer. For selecting appropriate values of thermal diffusivity, $D_e$ and $D_i$, the model output was compared and fitted to the normalized dynamic tip displacement of the 27 $\mu$m thick uniform PPy bi-layer actuator.

The combination of hole pitches and diameters investigated led to a range of maximum diffusion paths between 1.5 and 15.7 $\mu$m. Simulated response times ($\tau$) are plotted in figure 4(b). The model suggests an increasing rise time from $\tau = 13-30$ s with increasingly longer diffusion paths. Since a diffusion model was used, a square regression was fit to the simulated data to describe the trend, as shown by the solid line.

When compared to the rise time of 66 s of the uniform actuator, the model predicted a 4× improvement of the actuation speed with a simulated perforated actuator geometry that has an ion diffusion path of 1.54 $\mu$m or a hole diameter and pitch of 4 and 5 $\mu$m, respectively. By removing part of the polypyrrole volume for improved actuation speed, the actuator’s apparent stiffness should decrease, resulting in a decrease of the maximum obtainable curvature. The simulation results are shown in figure 4(c), where curvature is plotted ($\kappa$) against percent polypyrrole volume removed. The model predictions are seen most clearly in the inset. The results suggest a wide workable range of volume removal with almost negligible impact on curvature—suggesting that for the particular bilayer geometry used, it is free strain, rather than stress, that largely determined the degree of bending. This relative independence of volume fraction offers an opportunity to explore perforation for optimizing the actuation speed. Together, the simulation results in plots figures 4(b) and (c) suggest that actuator perforation can greatly improve the actuation speed while maintaining good bending outputs.

Relative change of modulus of layers in a bending bilayer is known to lead to a change in the degree of bending and in

![Figure 3](image-url)
the blocking force [28]. The change in curvature with change in modulus can be small, however. As the modulus of the active layer drops, the neutral axis moves away from the layer that is becoming more compliant, with the increased moment arm somewhat compensating for the drop in elastic stress. Furthermore, in the more porous films, volumetric charge transfer is higher than in the less porous ones, increasing free strain, and again compensating for the drop in modulus. As a result the effect of adding pores to the film, and thereby reducing the active layer stiffness, can be relatively small—as shown in the inset of figure 4(c).

3.3. Electrochemical characterizations

In the CV plot presented in figure 5, the voltage is ramped up at 2 mV s⁻¹, and then down again, and the resulting currents are measured. Scanning from −0.2 V to +0.2 V versus Ag/AgCl takes 200 s. Hole spacings and sizes are indicated in the caption, from which fill fraction and diffusion path length can be calculated. Fill fractions (meaning how much of the initial polypyrrole is left after machining) range between 0.42 and 1, while path lengths (longest path of ion diffusion), range from 4 to 27 mm. To understand the form of the CVs observed, it is important to understand that for simple capacitor of capacitance, \( C \), the current instantly rises to \( C \frac{dV}{dt} \), where \( \frac{dV}{dt} \) in this case is ±0.002 V s⁻¹ (positive currents for a positive scan direction). It is clear that for most samples a constant current is reached on the upward scan, as evidenced by the flatness of most of the curves as they approach the top right. All curves rise from negative current values off the start of the positive scan, and then flatten either to a constant current, or in a few cases, to a slowly rising current.
The blue curve—which is unperforated polypyrrole—is one of the ones still rising. This shows that a steady charging rate has not been reached, even after 400 s. In the cases where the current saturates, the capacitance per volume is found to be $2.1 \times 10^8 \text{ F m}^{-3}$ (accounting for the lost volume from the perforations), which is consistent with previously reported values for polypyrrole synthesized in the same way [11]. The electrochemical activity of the polypyrrole is not changed by laser machining. But what about the speed of response?

By inspection, it appears that the perforated samples show shorter rise times. It is also evident that there is a large variation in these times. The rise time is computed as the time taken for the current to reach $(1 - 1/e) = 0.63$ of the saturation current. Where saturation is not reached, the saturation current is estimated from the product of the volumetric capacitance, the sample volume and the scan rate. The rise times are plotted as a function of diffusion path length in figure 6. Time constants range from 2 to 38 s in the perforated samples, compared to 70 s in the untextured film. The reduction in time constant is substantially greater than expected based on the reduction in capacitance alone—by between 1.6 and 15 times. This confirms that the perforated samples show faster responses.

The perforated samples were expected to show a quadratic increase in time constant with transport path length. This

![Figure 5](image-url)

Figure 5. (a) Cyclic voltammetry plot of free standing polypyrrole films with various patterned hole and pitch specifications in comparison with a reference sample without any laser ablation (in blue). Noted on each curve is the associated effective diffusion length, $h$, and the percentage of polypyrrole left after machining, Fill. (b) The rise time, computed from the cyclic voltammogram in (a), plotted versus the effective diffusion distance, $h$. The point in the top right is the unperforated polypyrrole.
is not evident from the plot. There is significant variation, perhaps due to variations in electronic conductivity and contact resistance. Despite the variability, perforation led to faster charging—and so it is also expected to produce faster actuation. Recent work has focused on realizing so-called hybrid battery-supercapacitors to take advantage of the relatively high specific energy of a battery and the high power delivery offered by many supercapacitors [26, 27]. This is of high interests in energy storage applications in electric vehicles, smart electric grids, and other integrated energy management systems [28], whose electrode design might benefit from perforation.

3.4. Actuation tests

Video recordings of the bending actuators were processed and analyzed with MATLAB to extract the curvature, as shown in figure 6(b), for a laser-perforated actuator with a hole pitch of 14.9 μm and a hole diameter of 11.4 μm. The actuator was driven initially by a +0.6 V square wave of 240 s period for three cycles. The driving frequency was doubled in the remaining two cycles when the tip was observed to have reached the maximum position within 60 s. The curvature decreased gradually from 0.182 mm⁻¹ in the first cycle to 0.155 mm⁻¹ in the fifth cycle. This loss of output in the first few cycles is a known behavior of PPy-based actuators, which was attributed to unequal oxidation and reduction reaction in the polymer during voltage cycling [29]. Additionally, the data indicate a faster and relatively constant charging time versus an initially slower but shortening discharging time. However, the rise times averaged for both half cycles converged to within 5% in the fifth cycle at τ = 7.2 ± 0.2 s. Similar behaviors were observed across all actuators including the uniform actuator.

The experimental rise time of the perforated polypyrrole actuators (+s) are plotted together with the simulated values (x’s), as a function of ion diffusion path, in figure 4(b). The experimental data confirm the dramatic improvement in rate of charging achieved by perforation. The square law fit lines show an intercept, suggesting other rate limiting factors are at play, in addition to diffusion path length. Likely factors limiting the rate of charging in addition to the diffusion time through the active polymer, are solution resistance and contact resistance. These factors presumably contribute to the scatter in the measured results. From the regression, a 5.4× improvement of the actuation speed was obtained, at the smallest experimental ion diffusion path length of 1.1 μm. This improvement is relative to the rise time of 66 s in the unperforated sample. As with the electrochemical response, the largest improvement was by a factor of over thirty. This was from a pico-second laser machined sample with a pitch of 14.9 μm, a hole diameter of 11.9 μm, and an effective maximum diffusion length of 3.9 μm.

Figure 4(c) shows the maximum measured curvatures achieved by the bilayer actuators (+s). The average curvature is as expected from the simulation, but the variation in response is large. This variation is likely due to the differences in geometry introduced during the bilayer lamination process (polypyrrole films were manually applied onto Kapton tapes by hand)—since bending is very sensitive to beam thickness. While it is difficult to make firm conclusions, given the variability of the response, on average the output bending curvature is relatively unaffected by the laser perforation, up to the tested range of approximately 45% volume removal. We tentatively suggest the interpretation that the mechanical response follows the expectations of the model, with the degree of deflection being relatively constant over a range of perforation volume fractions. This will need to be confirmed through follow on work, in which the assembly process leads to a more uniform response.
4. Discussion

The perforation of the electrodes via laser micropatterning generated a significant increase in speed. To get further improvements from the electrodes used, other limiting factors include the finite ionic resistance of electrolyte that sits between electrodes, and the finite electrical resistance of the electrodes and contacts. These can be overcome by making better electrical contact, contact all along the polypyrrole (tricky without reducing bending), and by using thin separators between electrode. If these are overcome, how far can the hole perforation be used to push rates? The limiting factor will be the longest diffusion path length, $a$, with an associated time constant of $a^2/4D$. Using laser cutting, a 1 $\mu$m pitch is close to the practical limit, particularly in electrodes that are thick. In dense polypyrrole ($D \sim 10^{-12} \text{ m}^2 \text{s}^{-1}$), as used here, and given a hexagonal spacing, a time constant of about 0.5 s—about 4 times faster than the fastest actuator produced in our study—will be close to the limit. This fast response could alternatively be produced by using an electrode that is only a little over 1 $\mu$m thick. Such thin electrodes are often impractical however, because they are hard to handle. Also, energy density can be very low due to separators and packaging, which are typically much thicker.

Introducing porosity allows higher speed actuation in thick electrodes—but how much thicker can they be? That depends on the relative resistance of the pores—at some point the $RC$ time constant of the pore resistance multiplied by the electrode capacitance becomes dominant. Assuming an ionic conductivity of the pores of 1 $\text{S m}^{-1}$, a capacitance per volume of $10^8 \text{F m}^{-3}$ this suggests a maximum thickness of about 60 $\mu$m to achieve a 0.5 s time response [11]—a thickness that is easy to handle.

How can even faster charging be achieved? Adding nanoscale porosity using interpenetrating polymer networks is a proven approach in the conducting polymer PEDOT [14], and further development of chemistry may make this accessible to other electrodes. Here the interpenetration polymer used to create high ionic conductivity (polyethylene oxide) is not as conducting as free electrolyte, which then reduces the total electrode thickness for which the approach is viable. Combining microscopic pores such as those demonstrated in this study, with nano-sized interpenetrating ionic conductors such as those recently demonstrated, could together enable relatively thick electrode structures to charge quickly—benefitting actuators, but also batteries and supercapacitors. The main drawback of the approach—especially for battery and supercapacitor electrodes—is some loss of capacity per volume (20%–50% in the materials shown here). Also, as the machining process is serial in nature, the processing time could be significant in large area electrodes. Parallel laser machining, or even sink electrical discharge machining [23], should provide much faster processing for large area electrodes.

One aspect associated with perforation that needs further investigation is effect on performance of the loss of mechanical stiffness of the material, which is expected to be proportional to the solid volume fraction. This drop in modulus will lead to lower blocking forces, again in proportion to the volume fraction. Depending on the mechanical stiffness of the entire structure, it may also lead to a drop in bending displacement. There is a tradeoff between force/displacement and speed that should be borne in mind by device designers. Perforation may also reduce tensile strength. A reduction in tensile could have a particularly important effect on the maximum load and work density of linear conducting polymer actuators, which are films operating in tension. There is likely a much reduced effect in bilayer and trilayer structures due to the stabilizing influence of the passive layers.

5. Conclusions

Femto/pico second laser texturization is an effective means to improve actuation speed in polypyrrole. When compared with the response of the uniform actuator with identical thickness, an actuation speed improvement of 5 times on average, and up to 30 times, was experimentally measured in perforated actuator geometries. The fastest devices charged and actuated in a few seconds despite being thick (27 $\mu$m) and dense. This speed enhancement has significant implications for conducting polymer actuator designs, which typically reach high speeds by reducing actuator thickness and creating composite structures. The results could enable new designs of conducting polymer-actuated steerable catheters, microgrippers, and positioning systems. Furthermore, the demonstrated ability to reduce the ionic impedance without greatly reducing available charge storage could be applied to electrochemical energy storage devices, alleviating the tradeoffs between high speed charging on the one hand—often achieved by using thin electrodes—and electrode ease of handling, energy and capacity on the other.

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