

Rate Limits in Conducting Polymers

Tina Shoa^{1,2 a}, John D. Madden^{1,2 b}, Chi-Wah Eddie Fok^{1,2 c}, and Tissaphern Mirfakhrai^{1,2 d}

¹Department of Electrical & Computer Engineering, University of British Columbia, 2332 Main Mall, Vancouver, B.C. Canada, V6T 1Z4

²Advanced Materials and Process Engineering Laboratory, University of British Columbia, 2355 East Mall, Vancouver, B.C. Canada, V6T 1Z4

^atinass@ece.ubc.ca, ^bjmadden@ece.ubc.ca, ^ccfok@ece.ubc.ca, ^dtissa@ece.ubc.ca

Keywords: conjugated polymers, artificial muscle, carbon nanotube, diffusion, migration.

Abstract. Conducting polymer actuators are of interest in applications where low voltage and high work density are beneficial. These actuators are not particularly fast however, with time constants normally being greater than 1 second. Strain in these actuators is proportional to charge, with the rate of charging being found to limit the speed of actuation. This rate of charging is in turn limited by a number of factors, the dominant factor depending on the actuator and cell geometry, the potential range, the composition and the timescale of interest. Mechanisms that slow response can be as simple as the *RC* charging time arising from the actuator capacitance and the series resistances of the electrolyte and the contacts, or may involve polymer electronic or ionic conductivities, which can in turn be functions of potential. Diffusion can also be a factor. An approach is presented to help estimate the relative magnitudes of these rate limiting factors, thereby enabling actuator designs to be evaluated and optimized for a given application. The general approach discussed is also useful for analyzing rate limits in carbon nanotube actuators and other related technologies.

Introduction

Conducting polymers feature conjugated (alternating single/double) bonds on their backbones. As a consequence these materials behave as semiconductors in their neutral state, and, when their electrochemical state is changed (as occurs during actuation) can be doped such that the bandgap is filled and conductivity increases greatly (to $\sim 10^5$ S/m in polypyrrole [1]). This electrochemical doping process often involves removal of electrons from the polymer backbone. Charge within the polymer is balanced by the insertion of negatively charged dopant ions. The polymer generally swells when dopant ions are inserted [2].

A key advantage of conducting polymer actuators relative other contractile materials such as piezoelectrics, relaxor ferroelectric polymers and dielectric elastomers is their low voltage operation. Only about 2 V are needed to actuate them [3]. This low voltage operation, along with the high work density [4, 5] makes them attractive for use in medical applications. Active catheters are being investigated [6] for example. However, the speed of response is a problem, especially if rapid scanning of the catheter tip is needed in order to perform imaging. A key reason for the slow response is that the charge transfer is incredibly large – often involving 1 ion and electron for every three to four monomers [1, 7]. High charge transfer is associated with a high degree of swelling, but relatively large currents and a long charging time.

During the charging and actuation process the low frequency characteristics of the circuit often mimic the response of a capacitor (voltage linearly proportional to charge) [8]. The capacitance per unit volume is enormous – on the order of 100 F/cm^3 , about five orders of magnitude higher than in a tantalum capacitor. In some situations the polymer may behave more like a battery than a capacitor, but even when the behaviour is not purely capacitive, an effective capacitance can be estimated by dividing total charge transfer by change in voltage. The larger the effective capacitance, the more charge needs to be transferred for a given change in voltage, and the larger the current needs to be in order to obtain the transfer in a given period of time. In order to charge a

1 cm³ actuator to 1 volt, 100 C need to be transferred, or 100 A of current on average needs to be applied if the process is to occur in 1 s. The internal resistance of the actuator must be less than 10 mΩ in order to have a small enough RC time constant to perform the charging. Obtaining such a low resistance is not a trivial matter, particularly when ion motion is involved, and when the electronic conductivity can also be poor.

Conducting polymer actuators generally consist of two polymer electrodes, separated by an ionically conductive electrolyte, Figure 1. Transfer of electrons leads to transfer of ions to balance charge. These ions and perhaps also some solvent must squeeze between polymer chains, driven by concentration gradients (diffusion) or by field (migration). Ions must also be transported across the electrolyte, producing a resistive drop. These effects are considered in more detail in this paper, and means of estimating their influences are described. Also considered are the effects of resistive drop along the polymer.

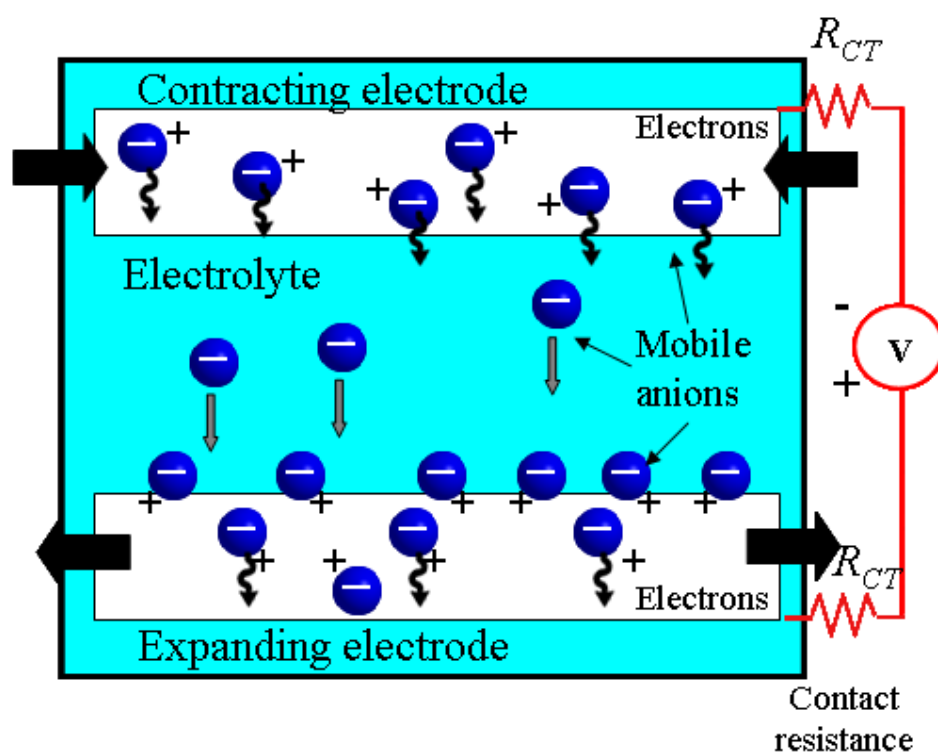


Fig. 1: Two polymer electrodes (white) to which voltage has been applied, leading at the bottom electrode to oxidation and incorporation of anions, leading in turn to swelling of the bottom electrode. The top electrode contracts as it is reduced and anions are expelled. The + signs represent positive charges on the backbone of the polymer. In the case shown the cations are not shown as they are assumed to be bulky and relatively immobile. In general the electrolyte can be selected so that anions, cations or both are involved in ionic charge transport.

The approach in this work is to employ RC and diffusion time constants to help determine rates of actuation. Other work on conducting polymer actuators has employed numerical models of voltage drops [9] and pressure driven solvent/ion flux [10]. In many cases numerical modeling is necessary due to the many factors that influence rate. In this work various analytical models are explored because, although sometimes simplistic, they are easier to relate to the underlying mechanisms of actuation.

The paper describes rate limiting mechanisms in terms of equivalent circuit models. The models are simplified in that they do not account for changing resistance as a function of oxidation state [11], but they do provide some insight into the rate limiting mechanisms. Some suggested means of increasing actuation rate are then presented.

Rate Limiting Mechanisms

Electrolyte Resistance and Ion Transport in the Polymer. As discussed the rate of charging determines the rate of strain, and can be limited by the rate of ion transport into the polymer. Figures 2a through 2c [12] show the steps involved in polymer charging. As shown in these figures a polymer electrode is in contact with an electrolyte phase and a counter electrode is placed on one side of the polymer. Assuming that only anions are mobile and are able to penetrate into the polymer, applying a voltage between the counter and the polymer electrode, Figure 2a, ions travel parallel to the applied field and concentrate at the polymer/electrolyte interface. The charges of the ions collecting at the electrode are balanced by the electronic charges on the polymer, forming what is known as a double layer capacitance, represented by, C . The ion transfer towards the interface is associated with a time delay imposed by the solution resistance (and any contact resistance), R_s , ($\tau = R_s C$). The ion flux changes the concentration of charge at the polymer surface, and creates a concentration gradient within the material which results in diffusing ions into the porous polymer (Figure 2b). There is also an electric field driving ions into the polymer which is likely to be significantly higher than the concentration dependent diffusion rates except at very low doping levels [7]. Ion diffusion into the polymer thickness is associated with a time delay which is determined by the effective diffusion coefficient, D , and the thickness, a , of the polymer (i.e. $\tau = a^2/D$). This diffusion like response holds whether the transport of ions is driven by concentration gradients or field gradients [13, 14], but in general the effective diffusion constant will be different for the two cases. Strain rate is directly proportional to current. At short times when concentration gradients and fields are relatively high, the diffusion-like transport is fast, and thus strain rate is also high. Eventually, the voltages and concentrations become uniform and mass transport ceases - or in other words the polymer is fully charged, Figure 2c. The charge is stored within the polymer volume, leading to a large effective capacitance, ($C_V \sim 10^8 \text{ F/m}^3$). The effective diffusion coefficient for field driven charging turns out to be $D_{eff} = \sigma_{ionic}/C_V$, where σ_{ionic} is the ionic conductivity of the polymer, and thus the mass transport limited time for charging through the thickness is $\tau = a^2 C_V / \sigma_{ionic}$. In hexafluorophosphate-doped polypyrrole this effective diffusion coefficient is thought to be approximately $10^{12} \text{ m}^2/\text{s}$, and is higher than the ‘concentration’ diffusion coefficient as measured by NMR [7].

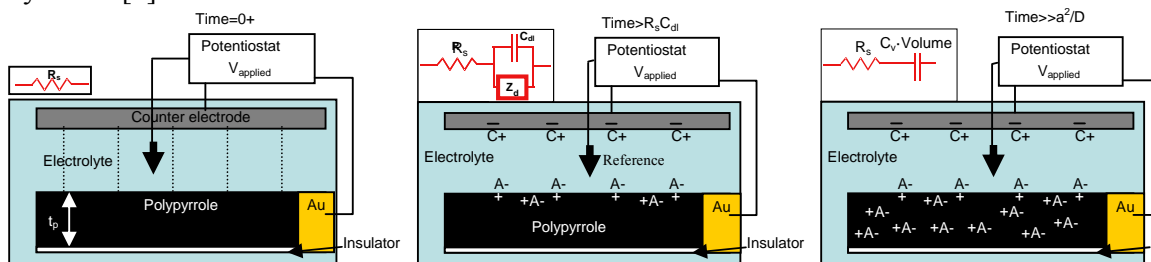


Fig. 2 Progression of conducting polymer charging, and the equivalent circuit as a function of time for a polypyrrole film immersed in an electrolyte containing mobile anions. (Left) A potential, $V_{applied}$, is applied between an electrode and a polypyrrole film, driving ions across the electrolyte. (Middle) The migration of anions leads to an accumulation of charge in the double layer at the polymer/electrolyte interface, having capacitance, C_{dl} . (Right) Charge is stored within the polypyrrole volume, with a volumetric capacitance, C_V .

The model shown above assumes high polymer electronic conductivity. Next the effect of the finite electronic conductivity of the polymer is considered. The electronic resistances of polymer segments, r_{ppy} , are added in the model shown in Fig. 3. The model shown assumes ion transport through the thickness (vertical direction) and voltage drops along the length (horizontal direction), with electrical contact to the polymer made from the ends. The transport of ions within the polymer is described by the finite transmission lines that extend vertically [11, 13, 14]. In this model, r_s is the solution resistance of a slice of solution between the working and counter electrodes, c_V is the polymer internal capacitance of a segment, and c is the double layer capacitance of a segment. Also depicted are the ionic resistances within segments polymer, represented by r_{ion} . In principle ionic resistances should also be shown in the length direction and electronic resistances through the

thickness. Electronic resistance, r_{ppy} , is not shown in the thickness direction because it is negligible compared to ionic resistance (e.g. $> 10^2$ S/m electronic, compared to 10^{-4} S/m ionic [7]). As a result the ionic charging will be the rate limiting mechanism through the thickness. The polymer electronic resistance can limit charging along the length in cases where the resistance is significant compared to the ionic resistance through the thickness. This occurs when the actuator is much longer than it is thick, so that even though the ionic conductivity is much lower than the electronic conductivity, the much shorter path length for ions means that at a certain distance from the ends of the actuator it is the rate of electronic transport that becomes the limiting factor.

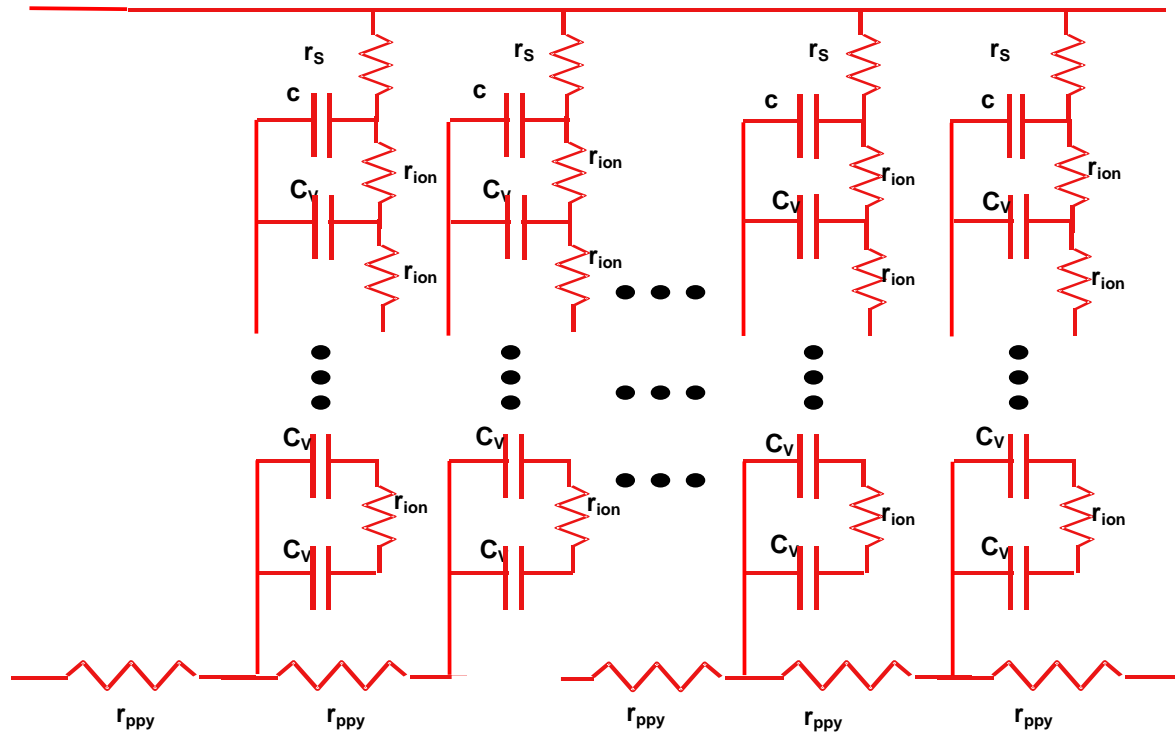


Fig. 3 Equivalent circuit model of a polymer film that is connected electrically at its ends, and exposed to an electrolyte on its upper surface, (where r_s represents the electrolyte resistance). Dots represent the repetition of the circuit elements. The capacitances lie at the interface between regions of electronic and ionic conductivity. In this model is assumed that the applied potential range is small enough that no significant parasitic reactions occur.

Actuation rate. Rate of actuation is primarily limited by the rate at which charge can be injected. As discussed, charge transfer is restricted by the internal resistance of the cell and by the rate at which ions are transferred within the polymer. If solution total resistance between electrodes, R_s , is large compared to other resistances, then this form of RC charging may be rate limiting, with the charging time constant is expressed as, $\tau = R_s C$ [13]. In this case C is the total capacitance of the polymer film, and equal to $C_V \cdot Volume$. For a long device the total polymer resistance along the length, l , of the catheter, R_{ppy} , can significantly limit the rate [15], with a time constant of $\tau = r_{ppy} C = \frac{C_V l^2}{\sigma}$ [13], where σ is the electronic conductivity of the polymer, and l is the polymer length. For a thick device the ionic resistance through the thickness, a , is rate limiting factor, with the time constant of $\tau = \frac{a^2 \cdot C_V}{\sigma_{ionic}}$ [13]. Ionic conductivity, like electronic conductivity, is likely a

function of oxidation state. In some situations thermally driven transport, which occurs in response to concentrations gradients, will dominate over field driven transport. If the effective mean free path of the ions, or alternatively the effective viscosity of the medium to ion motion, is the same for thermally driven motion as it is for field driven transport, then the concentration driven transport

will dominate when $k \cdot T \cdot C_V \gg q^2 \cdot N$, where k is Boltzmann's constant, T is absolute temperature, q is the charge on an ion, and N is the ion number density [7]. Thermal diffusion may be faster than field driven transport may be encountered in highly reduced polymer films.

The time constants discussed can be employed to help design and model fast polymer actuation. If any one of these time constants is much larger than the others, then the total charging time is dominated by this time and modeling is relatively simple. Otherwise multiple factors need to be accounted for. The preceding analysis is an oversimplification when multiple rate limiting mechanisms operate simultaneously. The discussion that follows proposes models to treat such situations.

After a relatively short time, t , only a fraction of the thickness of the polymer is accessible to mass transport. This thickness is can be estimated to be $a_{active} = \sqrt{\sigma_{ionic} \cdot t / C_V}$, assuming a diffusion like propagation of charge. Fig. 4 illustrates active thickness within the polymer as a function of time. At the beginning of the actuation (i.e. short times) ions can be inserted into only a portion of the thickness so we are assuming that only the outer a_{active} is involved in charge transfer and actuation. This analysis is not valid over voltage ranges where the ionic conductivity is varying

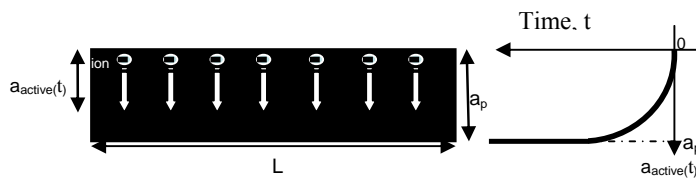


Fig. 4: Illustration of ion diffusion into the polymer thickness, as a function of time

substantially. In such cases a numerical model can be used, and the active region will advance as a constant velocity front under some circumstances [11]. Even when conductivity is relatively constant, the active thickness can also be dependent on position along the length of the polymer, particularly if voltage drop along the polymer is

significant. A model is next suggested to account for this effect.

The effective capacitance per unit length at any given position, l , along the polypyrrole film is given by $C_{eff}(l) = C_V \cdot w \cdot a_{active}(l)$, where w is the width of the polymer. At the beginning of the actuation (i.e. short times) only a length, $l=L_{active}$, of a device is responding to the applied voltage

due to the electronic delay (Fig. 5). The remaining polymer length does not significantly contribute to actuation. If the active thickness is fixed over a length L_{active} , then from the electronic RC charging time it is possible to estimate L_{active} :

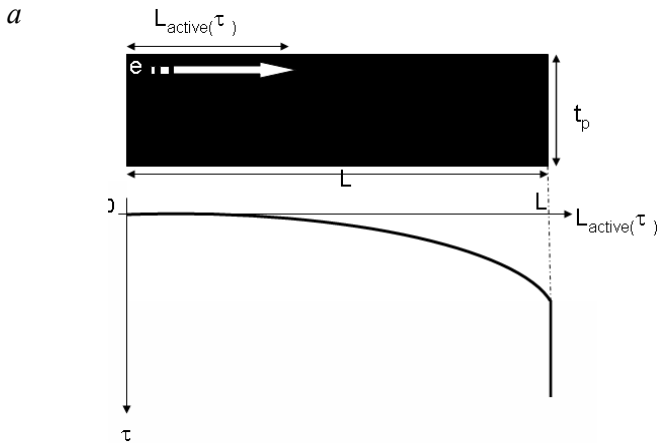


Figure 5: Electron propagation along the polymer length as a function of time, τ .

$$L_{active}(t) = \sqrt{\frac{\sigma \cdot t \cdot a}{C_V \cdot a_{active}(t)}} \quad \text{Eq. 1}$$

Fig. 6 illustrates this effect by showing the active regions at different times ($\tau_1 - \tau_5$). At τ_1 only the grey portion of the length which is attached to the contacting highly conductive electrode is active. At τ_2 blue regions are added and this trend continues till the entire length and thickness are eventually active.

Therefore a_{active} needs to be found for each successive active length as a function of time. Equation 6

estimates a_{active} as a function of time and length with L being an array representing positions along the polymer length.

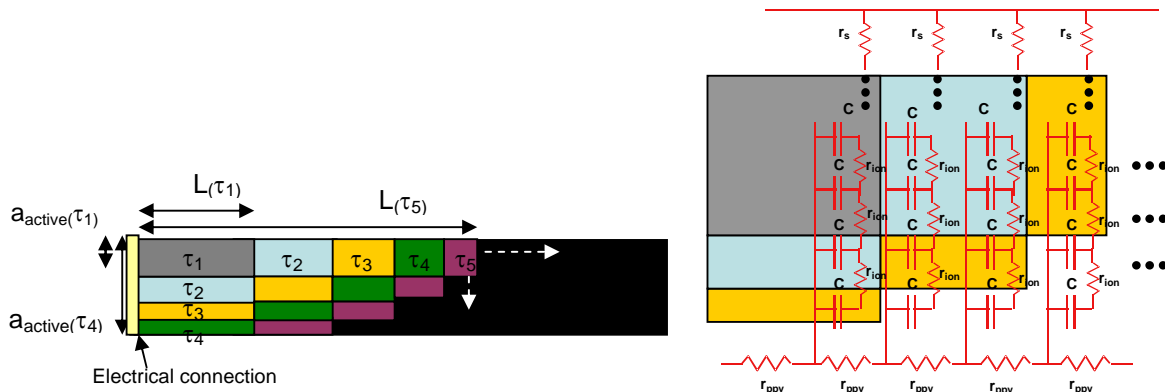


Fig. 6: Schematic of diffusion-like behaviour across the polymer length and thickness.

$$a_{active}(L, \tau) = \sqrt{D(\tau - \tau_{electronic}(L, \tau)) \cdot u(\tau - \tau_{electronic}(L, \tau))}, \text{ where}$$

$$\tau_{electronic}(L, \tau) = L \frac{C_v \cdot \sum_{k=1}^{\tau} [(L(k) - L(k-1)) \cdot a_{active}(\tau - k + 1)]}{\sigma \cdot a_p}. \quad \text{Eq. 2}$$

In this equation, $u(t)$ is the unit step function. This approach to estimating actuation can be effective providing that thermal diffusion is not significant. It also does not account for changes in conductivity that can take place when cycling is deep. In some conducting polymers capacitance will also be a function of oxidation state.

Increasing the speed of actuation

The actuation speed is limited by electronic, solution and ionic conductivities. We now turn to exploring how these rate limits can be overcome. Scaling down the dimensions is a good way to increase speed because it leads to shorter paths for electrons and ions to travel, with the time constant changing as the square of the critical dimension. Other approaches are to improve conductivity, apply potential in such a way as to optimize charging rate, and to make use of resonant structures. These approaches are now discussed.

Improving electronic conductivity. In order to increase electronic conductivity there are a number of approaches. Perhaps the simplest is to deposit a thin layer of gold or another metal on the polymer. This will reduce electronic delays, but the additional gold layer will add to the stiffness of the device and will make it more difficult for the active polypyrrole region to actuate the catheter. Creating a corrugated structure can reduce the impact on strain of this metal layer, or even lead to an enhancement in strain [16]. Incorporation of carbon nanotubes into the polymer structure has also been used to both increase conductivity and stress [5]. It can however lead to a reduction in strain.

Using Shaped Potential actuation. Controlled application of high potentials (that would normally degrade the polymer electrodes) has been shown to increase the actuation speed [17, 18]. This form of rate improvement is most useful when there is a relatively large resistance in series with the actuator. If the resistance across the electrolyte is high compared to the electronic and polymer ionic resistances, then using high voltages initially will help drive ions across the electrolyte, thereby charging the polymer – electrolyte double layer faster. Once the double layer is charged to the desired voltage, the applied voltage is reduced to avoid degradation. It is important to know the potential limits of the polymer actuator being used in order to effectively use this technique [19].

Improving ionic conductivity. The choice of dopant anion and solvent can improve the speed of response [20], with actuation in aqueous sodium hexafluorophosphate being much faster than in tetraethylammonium hexafluorophosphate solutions in propylene carbonate, for example [21].

Increasing the polymer porosity should also result in faster diffusion of ions into the polymer structure leading to a high ionic conductance [20]. Carbon nanotubes sheets, which are much more porous than conducting polymers, have been shown to have time constants for charging in the millisecond range [18].

Resonant Structures. Improvements in actuation speed and amplitude have also been achieved by making use of mechanical resonance amplification where the device is actuated at its resonance frequency [22]. Thus one possibility is to operate the catheter at its resonant frequency; thereby increasing displacement. This approach is useful where large, fast and periodic displacements are needed.

Conclusions

The rate of actuation of conducting polymers is generally limited by the rate of charging. The electronic and ionic resistances of the polymer and of the electrolyte can all be factors in limiting rate of charging. Diffusion can also be a factor. When these are combined with the high capacitance of the conducting polymers, the resulting time constants can be significant. These rate limiting mechanisms can be modeled using equivalent circuits. Linear models may prove to be effective providing the potential range is not sufficiently large to result in substantial changes in ionic and electronic conductivities. For deep charge/discharge, numerical models that account for such changes in properties are needed. Analysis of equivalent circuits suggest methods of improving rate, including reduction in size, increase in polymer electronic conductivity (e.g. by adding metals), increase in porosity, and the application of shaped potentials that enable the current limits imposed by series resistances to be overcome.

References

- [1] M. Yamaura, T. Hagiwara and K. Iwata, *Synthetic Metals*, 26, (1988), p. 209
- [2] Q. Pei and O. Inganäs, *Solid State Ionics*, 60, (1993), p. 161
- [3] J. D. W. Madden, N. A. Vandesteeg, P. A. Anquetil, P. G. A. Madden, A. Takshi, R. Z. Pytel, S. R. Lafontaine, P. A. Wieringa and I. W. Hunter, *Oceanic Engineering, IEEE Journal of*, 29, (2004), p. 706
- [4] G. M. Spinks and V. T. Truong, *Sensors and Actuators a-Physical*, 119, (2005), p. 455
- [5] G. M. Spinks, V. Mottaghitlab, M. Bahrami-Saniani, P. G. Whitten and G. G. Wallace, *Advanced Materials*, 18, (2006), p. 637
- [6] A. Mazzoldi and D. De Rossi, *Proceedings of the SPIE, Smart Structures and Materials*, 3987, (2000), p. 273
- [7] C.-H. Tso, J. D. Madden and C. A. Michal, *Synthetic Metals*, 157, (2007), p. 460
- [8] M. R. Warren and J. D. Madden, *Synthetic Metals*, 156, (2006), p. 724
- [9] X. Z. Wang, B. Shapiro and E. Smela, *Advanced Materials*, 16, (2004), p. 1605
- [10] A. Mazzoldi, A. Della Santa and D. De Rossi, "Conducting polymer actuators: Properties and modeling", *Polymer Sensors and Actuators Springer Verlag Heidelberg* (1999)
- [11] M. R. Warren and J. D. Madden, *Journal of Electroanalytical Chemistry*, 590, (2006), p. 76
- [12] J. D. Madden, *Conducting Polymer Actuators Massachusetts Institute of Technology Cambridge, MA* (2000)
- [13] J. D. Madden, P. G. Madden and I. W. Hunter, *Proceedings of SPIE*, 4695, (2002), p. pp. 176
- [14] J. D. Madden, P. G. Madden and I. W. Hunter, *Proceedings of SPIE*, 4329, (2001), p. 72
- [15] P. G. A. Madden, J. D. W. Madden, P. A. Anquetil, N. A. Vandesteeg and I. W. Hunter, *Oceanic Engineering, IEEE Journal of*, 29, (2004), p. 696
- [16] L. Bay, K. West, P. Sommer-Larsen, S. Skaarup and M. Benslimane, *Advanced Materials*, 15, (2003), p. 310

- [17] J. D. Madden, R. A. Cush, T. S. Kanigan and I. W. Hunter, *Synthetic Metals*, 113, (2000), p. 185
- [18] J. D. W. Madden, J. N. Barisci, P. A. Anquetil, G. M. Spinks, G. G. Wallace, R. H. Baughman and I. W. Hunter, *Advanced materials(Weinheim)*, 18, (2006), p. 870
- [19] T. Shoa, M. Cole, N. R. Munce, V. Yang and J. D. Madden, *Electroactive Polymer Actuators and Devices (EAPAD) 2007*, 6524, (2007), p. 652421
- [20] S. Hara, T. Zama, W. Takashima and K. Kaneto, *Synthetic Metals*, 149, (2005), p. 199
- [21] M. Cole and J. D. Madden, *Materials Research Society Fall Meeting*, 889, (2005), p. 105
- [22] G. M. Spinks, Y. Wu, G. Alici and G. G. Wallace, *Synthetic Metals*, 156, (2006), p. 1017