Chapter 11: Discussion and Conclusions

The electrochemical and mechanical properties of hexafluorophosphate-doped polypyrrole are studied. It is found that changes in oxidation state produce strains. Strain, ε , is reversible and directly proportional to the charge density transferred to the polymer, ρ , over a potential range of -0.8 V to +0.4 V vs. Ag/AgClO₄^{*}:

$$\varepsilon = \alpha \cdot \rho$$
, 1

where α is referred to as the strain to charge ratio. In propylene carbonate based tetraethylammonium hexafluorophosphate electrolytes, α =1.3±0.3×10⁻¹⁰ m³·C⁻¹ providing the uniaxial load on the polymer is less than 4 MPa. The strain resulting from a scan over this range of response is 2.3 %. The strain to charge ratio increases above 0.4 V vs. Ag/AgClO₄, such that reversible strains of 6 % are achieved. However, degradation is visible in this potential range. At potentials below –0.8 V vs. Ag/AgClO₄ the sign of the strain to charge reverses itself. At and above 4 MPa, the strain to charge ratio shows frequency dependence. The strain to charge ratio is unchanged from its lower load value at frequencies above 100 mHz, even at the highest measured stress of 34 MPa. Below 100 mHz the strain to charge ratio falls by 70 %. The strain to charge ratio increases to 3×10^{-10} m³·C⁻¹ in aqueous tetraethylammonium hexafluorophosphate electrolytes. The positive value of the strain to charge ratio is consistent with doping by

^{*} -0.1 V to +1.1 V vs. saturated calomel electrode (SCE).

hexafluorophosphate anions and exclusion of tetraethylammonium cations from the polymer.

Following some initial dynamics, the applied voltage, V, is also found to be directly proportional to the charge density, ρ :

$$V \cdot C_V = \rho , \qquad 2$$

between -0.1 V and +1.1 V vs. SCE, where C_V is the volumetric capacitance, measured to be $C_V=1.3\pm0.2\times10^8$ F·m³. In an 8.5 µm thick film, the phase of the frequency response indicates that 91 % of the input electrical energy is stored at 1 mHz. It appears that surface parasitic reactions and currents into the clamped film ends are primarily responsible for the 10% dissipation observed, and thus higher electrical energy storage proportions are obtainable if these currents are reduced.

Combining equations 1 and 2 provides a relationship between strain and voltage,

which applies after charging is complete.

A model is developed to explain the dynamics of the polymer charging. The model assumes a double layer capacitance at the polymer-electrolyte interface. The cell potential drop is the sum of the current induced drop across the electrolyte, and the potential across the double layer capacitance. Transport within the polymer is by diffusion of ion and charge pairs. The potential drop at the double layer provides energy to insert or remove dopant ions from the electrolyte. An electrical to mechanical coupling term is also included. The model is fit to frequency response data taken between 0.1 mHz and 100 kHz, from which diffusion coefficients are estimated. The 310

model and data agree within experimental uncertainty over the measured frequency range of 0.1 mHz and 100 kHz. At the frequency extremes, however, differences in the forms of the measured and predicted responses suggests that non-uniform charging may be occurring at high frequencies, and parasitic reactions at low frequencies.

The diffusion coefficients estimated from the model are in the range of 0.7 to 7×10^{-12} m²·s⁻¹, with the extent of variation resulting from differences between polymer samples. These differences are not correlated with film thickness. In older samples, mass transport into the polymer is negligible. Also, it is found that the rate of dopant transport is correlated with polymer solvent content. Upon immersion of polymer films into propylene carbonate electrolyte, swelling is observed. Rates of mass transport increase during swelling. It appears likely that the variations in the magnitude of the diffusion coefficient suggested by the model reflect real differences between films that result from aging or drying.

The porous metal theory, in which the electrochemical response of conducting polymers is attributed to charging of electrolyte filled pores, does not apply to the polypyrrole samples used in this study. A number of factors including the enormous magnitude of the capacitance, and the inability of large ions to penetrate polypyrrole, suggest that pores having sizes larger than several nanometers do not play a significant role in determining polymer charge transfer. The efficiency is a function of voltage, load and the strain to charge ratio. For example, the efficiency, e, obtained upon applying a step in applied voltage and under constant stress, σ , is calculated using the relationship:

$$e = \frac{2 \cdot \sigma \cdot \alpha}{V}, \qquad 4$$

when no stored electrical energy is recovered. Measured electrical to mechanical conversion efficiencies reach 3 ± 1 % at a loads of 30 MPa and at applied potentials of ± 0.1 V. The recovery of input electrical energy that is stored capacitively would lead to an efficiency of 7 ± 2 %.

Operation at 30 MPa is impractical because significant creep is observed after 1 to 10 s. Over 4000 seconds the creep reaches 0.5 %. At 3.5 MPa, creeps of 0.2 % are observed with a time constant of 30 s. Also, strain to charge ratio becomes independent of frequency below 4 MPa. Thus, for practical purposes, loads of less than 4 MPa are appropriate. Electrical to mechanical conversion efficiencies are less than 1 % at such loads assuming strains of at least 0.1 %. Thus, in order to obtain a 30 % electrical to mechanical conversion efficiency, more than 97 % of the electrical energy input needs to be recovered. While energy recovery of this magnitude has been obtained in conducting polymers (Baughman 1996), the best approach to maximizing efficiency is to investigate materials with much higher strain to charge ratios and/or load bearing capacities. The maximum strain rate achieved is $3\% \cdot s^{-1}$. Strain rate is determined by the rate of charge transfer to the polymer. Several factors limit the rate of charge transfer. No charge transfer will occur to the polymer at times shorter than the double layer charging time, τ_{RC} :

$$\tau_{RC} = R \cdot C \,, \qquad 5$$

where C is the double layer capacitance and R is the solution resistance. The solution resistance can be compensated for, however, as is done in Chapter 7, albeit at the expense of efficiency.

If the double layer charging time is made short by reducing resistance and capacitance, or is compensated for, the time taken for ions to initially diffuse into the polymer from the double layer determines the shortest time interval at which strain can be observed. The diffusive-elastic-metal model presented in Chapter 8 predicts that this time constant, τ_C , is:

$$\tau_C = \frac{\delta^2}{D}, \qquad 6$$

where D is the diffusion coefficient of ions within the polymer, and δ is the thickness of the double layer. Model fits to measured frequency responses suggest that $D \sim 10^{-12}$ m²·s⁻², and that $\delta \sim 1$ nm, predicting a maximum conceivable bandwidth of 10^5 Hz.

Once the double layer charging time and the minimum diffusion time are exceeded, then either the electrolyte resistance or the rate of diffusion limits polymer charging time and hence strain rate. The diffusion charging time constant is:

$$\tau_D = \frac{a^2}{4 \cdot D}, \qquad \qquad 7$$

where *a* is polymer film thickness. (The factor of 4 is removed if ions can only enter from one side of the thinnest dimension.). The volumetric $R \cdot C$ charging time, τ_{RCV} is:

$$\tau_{RCV} = R \cdot C_V \cdot V_P, \qquad 8$$

where V_P is polymer volume and C_V is the volumetric capacitance per unit volume, as in Equations 2 and 3. In cases where the diffusion time constant is much shorter than the volumetric charging time constant, strain rate is improved by reducing resistance and polymer volume. Where diffusion is rate-limiting, strain rate is proportional to the inverse square of polymer thickness, and therefore reducing polymer dimensions is very effective in increasing strain rate. Experimental evidence shows a reduction in charging time with film thickness, but also indicates that the diffusion coefficient is not constant between samples. If the mechanisms that the determine diffusion coefficient can be determined, this presents another means of improving response time.

Note that in the analysis of factors affecting strain rate it has been assumed that polymer resistance is small compared to solution resistance, and that the electronic carrier mobility is much higher than the mobility of dopants within the polymer. The first assumption is geometry dependent, and will not be met in long fibers and films, unless electrical contact can be made at points along their length. Designers of mechanisms

employing conducting polymer actuators must carefully consider film dimensions. The second assumption is dependent on synthesis conditions and oxidation state.

The various factors that determine strain rate in conducting polymers suggest employing short lengths of thin polymer in highly conductive electrolytes will minimize response time. The natural application of this technology is in micro and nano-devices, and efforts in this direction are already underway (Jager, Inganas and Lundstrom 2000). It is conceivable that the 10^5 Hz limiting bandwidth will be approached in microdevices. The power to mass ratio of 39 W·kg⁻¹ already exceeds the 20 W·kg⁻¹ of electrostatic actuators commonly used in micro-devices (Hunter and Lafontaine 1992), and promises to greatly exceed them. The forces that can be generated by conducting polymers exceed those of electrostatic actuators by two to three orders of magnitude, for a given actuator crosssection. If widespread application of conducting polymer actuators in microdevices is to occur, the methods of operating actuators outside a liquid environment presented in Chapters 6 and 7 will be important. As discussed in the introduction, entire autonomous microdevices might be made from a single conducting polymer, due to the great diversity of characteristics of these materials.

High power macroscopic motors driven by polypyrrole actuators will require microstructured components. If the 1 kW·kg⁻¹ power to mass ratio of the internal combustion engine is to be reached, then assuming diffusion limited behavior, and based on a diffusion coefficient of 10^{-12} m²·s⁻¹, the polymer film thickness required is ~200 nm for full contraction.

Future research into polypyrrole, and indeed other conducting polymer actuators, must determine factors influencing lifetime. Thus far, the maximum number of cycles reported

is 10⁵ (Chapter 7), but it is not known what the ultimate limits are, or what determines them. Other aims should be to maximize the strain to charge ratio and/or increase the load carrying capacity. These will increase the electrical to mechanical coupling, thereby enabling higher efficiencies to be attained. Investigation of molecules, which undergo large reversible conformational changes in response to oxidation or reduction, might enable strains of 20 % or more to be obtained, matching muscle. Such an advance would broaden the application of contractile actuators, because the need for mechanical advantage to amplify displacements is reduced.

11.1 Reference List

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